Environment Canada Environnement Canada

Final Screening Assessment
Petroleum Sector Stream Approach

Fuel Oil, No. 4
Fuel Oil, No. 6
Fuel Oil, Residual
[Fuels]

Chemical Abstracts Service Registry Numbers
68476-31-3
68553-00-4
68476-33-5

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Synopsis

The Ministers of the Environment and of Health have conducted a screening assessment of the following heavy fuel oils:

CAS RN[a]	DSL[b] name
68476-31-3	Fuel Oil, No. 4
68553-00-4	Fuel Oil, No. 6
68476-33-5	Fuel Oil, Residual

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[b] *Domestic Substances List*.

Fuel Oil No. 4 and Fuel Oil No. 6 were identified as high priorities for action during the categorization of the DSL, as they were determined to present greatest potential or intermediate potential for exposure of individuals in Canada, and were considered to present a high hazard to human health. Fuel Oil No. 4 and Fuel Oil No. 6 also met the ecological categorization criteria for persistence or bioaccumulation potential and inherent toxicity to aquatic organisms. Residual Fuel Oil was considered to present a high hazard to human health but low potential for exposure, and was included in this assessment because its composition and properties are similar to those of Fuel Oil No. 4 and Fuel Oil No. 6. These substances were included in the Petroleum Sector Stream Approach (PSSA) because they are related to the petroleum sector and are considered to be of Unknown or Variable composition, Complex reaction products or Biological materials (UVCBs).

These substances are transported in large volumes from refinery and upgrader facilities to other industrial end users such as pulp mills and large-scale power generation utilities via pipeline, ship, train and truck; therefore, exposure to the environment is expected.

An analysis of Canadian fuel oil spills data for the years 2000–2009 indicated that, on average, fewer than 1 spill per year occurs of sufficient size to be expected to be harmful to aquatic organisms (fish, invertebrates, algae) in marine waters around loading/unloading wharves.

While releases of Fuel Oil No. 4, Fuel Oil No. 6 or Residual Fuel Oil have the potential to have detrimental effects on aquatic birds, risk to birds is considered to be low due to the very low frequency of spills during transport.

Considering all available lines of evidence presented in this screening assessment, there is low risk of harm to organisms and the broader integrity of

the environment from these substances. It is concluded that Fuel Oil No. 4, Fuel Oil No. 6 and Residual Fuel Oil (CAS RNs 68476-31-3, 68553-00-4 and 68476-33-5) do not meet the criteria under paragraphs 64(*a*) or (*b*) of the *Canadian Environmental Protection Act, 1999* (CEPA 1999), as they are not entering the environment in quantities or concentrations or under conditions that have or may have immediate or long-term harmful effects on the environment or its biological diversity, or that constitute or may constitute a danger to the environment on which life depends.

A critical health effect for the initial categorization of these substances was carcinogenicity, based primarily on classifications by international agencies. Skin painting studies in laboratory animals reported skin tumour development after chronic dermal exposure to Fuel Oil No. 4, Residual Fuel Oil and related heavy fuel oil (HFO) substances. Limited *in vitro* genotoxicity studies were negative for Fuel Oil No. 4 and Fuel Oil No. 6, although other HFOs demonstrated genotoxicity. Dermal studies in laboratory animals of related HFO substances reported reproductive and developmental effects.

The potential for exposure of the general population to Fuel Oil No. 4, Fuel Oil No. 6 and Residual Fuel Oil was assessed. There is limited residential use and restricted access to these fuels; therefore, exposure of the general population is not expected. Thus, the risk to human health is considered to be low. Accordingly, it is concluded that Fuel Oil No. 4, Fuel Oil No. 6 and Residual Fuel Oil (CAS RNs 68476-31-3, 68553-00-4 and 68476-33-5) do not meet the criteria under paragraph 64(*c*) of CEPA 1999, as they are not entering the environment in a quantity or concentration or under conditions that constitute or may constitute a danger in Canada to human life or health.

It is therefore concluded that Fuel Oil No. 4, Fuel Oil No. 6 and Residual Fuel Oil (CAS RNs 68476-31-3, 68553-00-4 and 68476-33-5) do not meet any of the criteria set out in section 64 of CEPA 1999.

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1. Introduction

The *Canadian Environmental Protection Act, 1999* (CEPA 1999) (Canada 1999) requires the Minister of the Environment and the Minister of Health to conduct screening assessments of substances that have met the categorization criteria set out in the Act to determine whether these substances present or may present a risk to the environment or human health.

Based on the information obtained through the categorization process, the Ministers identified a number of substances as high priorities for action. These include substances that

- met all of the ecological categorization criteria, including persistence (P), bioaccumulation potential (B) and inherent toxicity to aquatic organisms (iT), and were believed to be in commerce in Canada; and/or
- met the categorization criteria for greatest potential for exposure (GPE) or presented an intermediate potential for exposure (IPE), and had been identified as posing a high hazard to human health based on classifications by other national or international agencies for carcinogenicity, genotoxicity, developmental toxicity or reproductive toxicity.

A key element of the Government of Canada's Chemicals Management Plan (CMP) is the Petroleum Sector Stream Approach (PSSA), which involves the assessment of approximately 160 petroleum substances that are considered high priorities for action. These substances are primarily related to the petroleum sector and are considered to be of Unknown or Variable composition, Complex reaction products or Biological materials (UVCBs).

Screening assessments focus on information critical to determining whether a substance meets the criteria set out in section 64 of CEPA 1999. Screening assessments examine scientific information and develop conclusions by incorporating a weight-of-evidence approach and precaution.[1]

[1] A determination of whether one or more of the criteria of section 64 are met is based upon an assessment of potential risks to the environment and/or to human health associated with exposures in the general environment. For humans, this includes, but is not limited to, exposures from ambient and indoor air, drinking water, foodstuffs and the use of consumer products. A conclusion under CEPA 1999 on the substances in the Chemicals Management Plan (CMP) Challenge is not relevant to, nor does it preclude, an assessment against the hazard criteria for the Workplace Hazardous Materials Information System (WHMIS) that are specified in the *Controlled Products Regulations* for products intended for workplace use. Similarly, a conclusion based on the criteria contained in section 64 of CEPA 1999 does not preclude actions being undertaken in other sections of CEPA 1999 or other Acts.

1.1 Grouping of Petroleum Substances

The high-priority petroleum substances fall into nine groups of substances based on similarities in production, toxicity and physical-chemical properties (Table A-1 in Appendix A). In order to conduct the screening assessments, each high-priority petroleum substance was placed into one of five categories ("Streams") depending on its production and uses in Canada:

> Stream 0: substances not produced by the petroleum sector and/or not in commerce
> Stream 1: site-restricted substances, which are substances that are not expected to be transported off refinery, upgrader or natural gas processing facility sites[2]
> Stream 2: industry-restricted substances, which are substances that may leave a petroleum-sector facility and may be transported to other industrial facilities (for example, for use as a feedstock, fuel or blending component), but that do not reach the public market in the form originally acquired
> Stream 3: substances that are primarily used by industries and consumers as fuels
> Stream 4: substances that may be present in products available to the consumer

An analysis of the available data determined that 13 petroleum substances are fuels under Stream 3, as described above. These substances were grouped according to fuel type as follows: gasoline; diesel fuels; Fuel Oil No. 2; Fuel Oil No. 4, Fuel Oil No. 6 and Residual Fuel Oil; and aviation fuels. The Stream 3 fuels occur within three of the nine substance groups: heavy fuel oils (HFOs), gas oils and low boiling point naphthas. The fuel oil substances considered in this assessment are HFOs.

Seven site-restricted HFOs were previously assessed under PSSA Stream 1 (Environment Canada, Health Canada 2011) and five industry-restricted HFOs were assessed under PSSA Stream 2 (Environment Canada, Health Canada 2013).

This screening assessment addresses three HFOs described under Chemical Abstracts Service Registry Numbers (CAS RNs) 68476-31-3 (Fuel Oil No. 4), 68553-00-4 (Fuel Oil No. 6) and 68476-33-5 (Residual Fuel Oil). Fuel Oil No. 4 and Fuel Oil No. 6 were identified as GPE or IPE during the categorization exercise, and were considered to present a high hazard to human health. These substances also met the ecological categorization criteria for persistence or bioaccumulation potential and inherent toxicity to aquatic organisms. Residual

[2] For the purposes of the screening assessment of PSSA substances, a site is defined as the boundaries of the property where a facility is located.

Fuel Oil was considered to present a high hazard to human health but low potential for exposure during the categorization exercise, and the ecological categorization for persistence, bioaccumulation potential and inherent toxicity to aquatic organisms was uncertain. However, Residual Fuel Oil was included in this assessment because it has similar composition and properties to Fuel Oil No. 4 and Fuel Oil No. 6.

Included in this screening assessment is the consideration of information on chemical properties, uses, exposure and effects. Data relevant to the screening assessment of these substances were identified in original literature, review and assessment documents, stakeholder research reports and from recent literature searches, up to February 2011 for the environmental section of the document, and up to September 2011 for the health effects section of the document. Key studies were critically evaluated, and modelling results were used to develop the conclusions.

Characterizing risk to the environment involves consideration of data relevant to environmental behaviour, persistence, bioaccumulation and toxicity, combined with an estimation of exposure to potentially affected non-human organisms from the major sources of releases to the environment. To predict the overall environmental behaviour and properties of complex substances such as these HFOs, representative structures were selected from each chemical class contained within these substances. Conclusions about the risk to the environment were based, in part, on estimation of environmental concentrations resulting from releases, and the potential for these concentrations to have a negative impact on non-human organisms. Other lines of evidence including fate, temporal/spatial presence in the environment and hazardous properties of the substances were also taken into consideration. The ecological portion of the screening assessment summarizes the most pertinent data on environmental behaviour and effects, and does not represent an exhaustive or critical review of all available data. Environmental models and comparisons with similar petroleum substances assisted in the assessment.

Evaluation of risk to human health involved consideration of data relevant to the estimation of exposure of the general population, as well as information on health effects. Health effects were assessed using pooled toxicological data from HFOs and related substances, as well as for high-hazard components expected to be present in the fuels. Decisions for risk to human health were based on the nature of the critical effect and margins between conservative effect levels and estimates of exposure, taking into account confidence in the completeness of the identified databases on both exposure and effects, within a screening assessment context. The screening assessment does not represent an exhaustive or critical review of all available data. Rather, it presents a summary of the critical information upon which the conclusion is based.

This screening assessment was prepared by staff in the Existing Substances Programs at Health Canada and Environment Canada and incorporates input from other programs within these departments. The human health and ecological portions of this assessment have undergone external written peer review/consultation. Comments on the technical portions relevant to human health were received from scientific experts selected and directed by Toxicology Excellence for Risk Assessment (TERA), including Dr. Bob Benson (United States Environmental Protection Agency [U.S. EPA]), Dr. Michael Jayjock (The LifeLine Group), Dr. Mark Whitten (Professor (retired) of Pediatrics, University of Arizona College of Medicine), and Dr. Errol Zeiger (Errol Zeiger Consulting). While external comments were taken into consideration, the final content and outcome of the screening assessment remain the responsibility of Health Canada and Environment Canada.

The critical information and considerations upon which the screening assessment is based are summarized below.

2. Substance Identity

The physical-chemical definition of HFOs includes the substances Fuel Oil No. 4, Fuel Oil No. 5, and Fuel Oil No. 6 (Fuel Oil No. 6 is commonly referred to as Bunker C, Bunker C fuel, Bunker C oil, Bunker C fuel oil, or simply Bunker) (Statistics Canada 2007). Residual Fuel Oil is a general classification for the heavier oils that remain after the distillate fuel oils and lighter hydrocarbons have been distilled in refinery operations and blended. Fuel Oil No. 5 and Fuel Oil No. 6 (and sometimes Fuel Oil No. 4) can be referred to as Residual Fuel Oil or HFOs. However, the Domestic Substances List (DSL) uses Residual Fuel Oil to refer to CAS RN 68476-33-5 (also called Fuel Oil No. 5 by industry and users). Therefore, the identity, description and likely composition of the three CAS RNs considered in this assessment can be unclear due to generic and inconsistent naming. Thus, to avoid confusion, and for the purposes of this report, Fuel Oil No. 4, Fuel Oil No. 6 and Residual Fuel Oil will be referred to collectively as HFOs.

Fuel Oil No. 4 (CAS RN 68476-31-3) is a residual fuel oil that is manufactured by the addition of blending stocks to distillation residues in order to meet viscosity specifications set by the American Society for Testing and Materials (ASTM) (ATSDR 1995). It is created by blending a distillate such as Fuel Oil No. 2 with a residual fuel oil or Fuel Oil No. 6 (HESS 2006a; personal communication, phone conversation May 28, 2010, between Shell Canada and Oil, Gas and Alternative Energy Division, Enivornment Canada, unreferenced).

Fuel Oil No. 6 (CAS RN 68553-00-4) (or Bunker C) is a specific type of residual fuel oil that is a complex combination of high molecular weight components with

a typical boiling point range of 160–723°C (API 2004). The typical carbon range of this fuel is between C_{20} and C_{50}, and mainly includes aliphatic, aromatic and cycloalkane hydrocarbons. It also includes some asphaltenes and smaller amounts of heterocyclic components that include sulphur, nitrogen and/or oxygen (CONCAWE 1998). Fuel Oil No. 6 is produced by blending residual fuel oils with lighter fuels or diesels in various ratios to yield a fuel of a specified viscosity as required by the user (Wang et al. 1999).

Residual Fuel Oil (CAS RN 68476-33-5) is a complex combination of petroleum hydrocarbons from various refinery streams; it varies with the source of crude oil (CONCAWE 1998). While some refineries label this CAS RN Fuel Oil No. 5 (HESS 2006b), others refer to it as Fuel Oil No. 6 but identify in its compositional information that it consists of 100% Residual Fuel Oil (this may be CAS RN 68476-33-5, or the refineries may be simply referring to the composition in general as Residual Fuel Oil) (NOVA Chemicals 2013). For the purposes of this report, Residual Fuel Oil (CAS RN 68476-33-5) will be considered the same as Fuel Oil No. 5. Typically, Fuel Oil No. 5 is prepared by combining 20–25% Fuel Oil No. 2 with 75–80% Fuel Oil No. 6 (Irwin et al. 1997).

These UVCB substances are complex combinations of hydrocarbon molecules that originate in nature or are the result of chemical reactions and processes that take place during the upgrading and refining process. Given their complex and variable compositions, they could not practicably be formed by simply combining individual constituents.

Of the three HFOs considered in this screening assessment, Fuel Oil No. 6 is the most readily available in Canada (Statistics Canada 2010). Fuel Oil No. 4 is not typically produced in large quantities by refineries, and it has been confirmed by industry as being a special-request product. Similarly, there is limited information on the production and transportation of Residual Fuel Oil.

A general hydrocarbon characterization of the HFOs is shown in Table 2-1. Relatively few data exist on the characterization of Fuel Oil No. 4 and Residual Fuel Oil.

Table 2-1. Characterization of Fuel Oil No. 4, Residual Fuel Oil and Fuel Oil No. 6 (Environment Canada c2001)

Hydrocarbon group	Fuel Oil No. 4	Residual Fuel Oil[a]	Fuel Oil No. 6[b]
Alkanes (wt %)	ND[c]	44.2	24–42.5
Aromatics (wt %)	ND	39.5	29–55
Resins[d] (wt %)	ND	8	15–17
Asphaltenes[e] (wt %)	3	8.4	6–19
Waxes[f] (wt %)	6	2.3	2–12
Total BTEX[g] (ppm)	ND	890	30–630
Total VOC[h] (ppm)	ND	2640	38–1570

[a] Cited as Fuel Oil No. 5 in the report.
[b] Ranges obtained from samples Bunker C Fuel Oil (Alaska), Bunker C Fuel Oil, Bunker C (Irving Whale), Heavy Fuel Oil 6303 and Bunker C Light Fuel Oil (Environment Canada c2001).
[c] ND: not determined or was not characterized in the reference noted.
[d] Resins are polar, heterocyclic molecules containing oxygen, nitrogen or sulphur (NRC 1985).
[e] Asphaltenes are an extremely complex, heterogeneous and poorly characterized assortment of components with high molecular weights, and low volatility and solubility (NRC 1985).
[f] Long-chain alkanes.
[g] BTEX: benzene, toluene, ethylbenzene and xylenes.
[h] Volatile organic compounds.

In 2008, the Alberta Research Council Inc. conducted a characterization of three samples of Fuel Oil No. 6 from Canadian refineries (Fuhr 2008). The combined compositional data on these samples are shown in Table 2-2.

Table 2-2. Fuel Oil No. 6 compositional data (three samples) (Fuhr 2008)

Hydrocarbon type	Range (wt %)	Average (wt %)
Saturates	**13–24**	**19.1**
Alkanes	3–8	4.9
Cycloalkanes	6–9	7.4
Aromatics	**35–50**	**43.4**
Monoaromatics	4–9	5.8
Diaromatics	3–9	7.0
Triaromatics	1–5	3.1
Tetraaromatics	2–3	2.4
Pentaaromatics	0.2–0.4	0.3
Unidentified aromatics	0.4–0.7	0.5
Aromatic sulphurs	1–2	1.3
Olefins	**0–0.2**	**0.1**
Polars	**22–29**	**25.2**
Asphaltenes	**4–19**	**12.2**
Total[a]	**100**	**100**

[a] Includes total saturates, aromatics, olefins, polars and asphaltenes (wt %).

As expected, aromatic hydrocarbons were predominant in the Fuel Oil No. 6 samples, and there was a lower content of saturated hydrocarbons than what is found in lighter fuel oil grades. The samples were also skewed toward the heavier hydrocarbons, with 64–68% of the weight having a boiling point greater than 500°C, and 2–4% of the weight with a boiling point below 200°C. These results are similar to a Fuel Oil No. 6 component analysis conducted by ATSDR (1999).

3. Physical-Chemical Properties

Fuel Oil No. 4, Fuel Oil No. 6 and Residual Fuel Oil are complex combinations of petroleum hydrocarbons that have varying physical-chemical properties depending on the crude oil source, the production year, and the blending ratios of the final fuels (Wang et al. 1999). A summary of physical-chemical properties of these HFOs is presented in Table 3-1. The data are taken from numerous sources and are therefore generally representative. As relatively few data exist describing the physical-chemical properties of Fuel Oil No. 4 and Residual Fuel Oil, it is considered that they are intermediate in properties between Fuel Oil No. 2 and Fuel Oil No. 6 (blending streams used to create these final fuels). Thus, Table 3-1 primarily focuses on Fuel Oil No. 6.

Table 3-1. Physical-chemical properties of Fuel Oil No. 4, Fuel Oil No. 6 and Residual Fuel Oil

Property	Value (substance)	Temperature (°C)	Reference
Pour point (°C)	-2–15	-	API 2004
Boiling point (°C)	101–588 (Fuel Oil No. 4) 160–723 (Fuel Oil No. 6) 160–600 (Residual Fuel Oil)	-	ATSDR 1995 API 2004 API 2004
Density (g/mL)	0.95–1.01 (Fuel Oil No. 6) 0.98 (Fuel Oil No. 6)[a]	15 20	CONCAWE 1998 Environment Canada c2001
Vapour pressure (Pa)	100 (Fuel Oil No. 6) 133–2000 (Residual Fuel Oil/Fuel Oil No. 6)[b]	20 20	North Atlantic Refining Ltd 2010 NOVA Chemicals 2013
Water solubility (mg/L)	0.4–6.3 (Fuel Oil No. 6)	22	API 2004
Log K_{ow} (dimensionless)	3.3–7.06 (Fuel Oil No. 6)	--	ATSDR 1995

	2.7– > 6 (Fuel Oil No. 6)		CONCAWE 1998
Log K_{oc} (dimensionless)	3.0–6.7 (Fuel Oil No. 6)	--	ATSDR 1995
Henry's Law constant ($Pa \cdot m^3/mol$)	6×10^{-5}–7.4 (Fuel Oil No. 6)	20	Oak Ridge National Laboratory 1989

[a] From entry for Bunker C Fuel Oil (Irving Whale)
[b] NOVA Chemicals identifies the substance as Residual Fuel Oil (CAS RN 68476-33-5) but lists Fuel Oil No. 6 as a synonym for the substance.
K_{oc}: organic carbon-water partition coefficient.
K_{ow}: octanol-water partition coefficient.

Water solubilities of all HFOs are low, and the octanol-water partition coefficient estimations vary considerably, likely due to the complex and variable nature of these mixtures.

Fuel Oil No. 4, Fuel Oil No. 6 and Residual Fuel Oil have low American Petroleum Institute (API) gravities, such that the specific gravity (0.95– > 1.03) can be less than or equal to that of fresh water (1.00) (NOAA 2010). The pour point of a petroleum product is the temperature below which the oil does not flow freely, as there will be crystallization of some components (Ford 1970). With a pour point of -2 to 15°C, spills of these HFOs in waters below 15°C would likely result in the formation of a semi-solid that would not disperse very readily. Thus, in water, these HFOs can sink, float or be neutrally buoyant depending on site-specific characteristics (the salinity and temperature of the water) and properties of the oil (NOAA 2010).

To predict the environmental behaviour and fate of a complex petroleum product such as these HFOs, representative structures were selected from each chemical class contained within the substances. Forty-five structures were selected from a database in PETROTOX (2009) based on boiling point ranges for each HFO (Table B-1 in Appendix B), the amount of data available on each structure, and the middle of the boiling point range of similar structures. As the compositions of most HFOs are not well defined and are variable, representative structures could not be chosen based on their proportion in the substances. This resulted in the selection of representative structures for alkanes, isoalkanes, one-ring and two-ring cycloalkanes, polycycloalkanes, cycloalkane monoaromatics, cycloalkane diaromatics, and one-, two-, three-, four-, five- and six-ring aromatics ranging from C_{12} to C_{50} (Table B-1 in Appendix B). Physical-chemical data for each representative structure were assembled from scientific literature and from the EPI Suite (2008) group of environmental models (Table B-1 in Appendix B).

While Table B-1 (Appendix B) provides physical-chemical property data for the individual structures, it should be noted that some of these properties will differ when the substances are present in a mixture, such as the HFOs. The vapour pressures of components of a mixture will be lower than their individual vapour

pressures due to Raoult's Law (the total vapour pressure of an ideal mixture is proportional to the sum of the vapour pressures of the mole fractions of each individual component). Similar to Raoult's Law, the water solubilities of components in a mixture are lower than when they are present individually (Banerjee 1984). Concurrently, however, components that are normally solid under environmental conditions may have lower melting points (and therefore be in a liquid state) and increased vapour pressure and water solubility when part of a mixture (Banerjee 1984). This is not reflected in Table B-1.

4. Sources

Fuel oil is produced by refineries across Canada (Statistics Canada 2007). Canadian refinery production of Fuel Oil No. 4, Residual Fuel Oil and Fuel Oil No. 6 (collectively defined as HFOs by Statistics Canada) was approximately 8258 million litres in 2008 (Statistics Canada 2009; Table C-1a in Appendix C). About 55% of Canadian production was exported (4550 million litres) and 1767 million litres of the three substances were imported (Statistics Canada 2009; Table C-1a in Appendix C). The Atlantic provinces collectively have the highest refinery production of these three substances at 46% of the Canadian total, followed by Quebec (32%) (Statistics Canada 2009;Table C-1a in Appendix C). The Atlantic provinces also have the highest exports compared to the other provinces (2784 megalitres). Environment Canada (2008, 2009, 2010b) also compiles data submitted by producers and importers of liquid fuels in Canada pursuant to the requirements of the federal *Fuels Information Regulations, No. 1*. Data with regard to HFO production and imports in Canada from 2006 to 2008 are shown in Table C-1b (Appendix C). The data show that there was an overall increase in HFO production and imports available for sale between 2006 and 2007, followed by a decrease in 2008 (Table C-1b in Appendix C). Variances between Environment Canada and Statistics Canada data may be a result of differences in approaches used to determine volumes (Environment Canada 2010). For example, volumes reported to Environment Canada mostly reflect production at various refineries, while Statistics Canada considers opening and closing inventories and inter-product transfers (Environment Canada 2010).

Product terminals receive petroleum products, including HFOs, and hold these products in storage for customers. These customers include wholesale distributors and bulk plants. HFOs are moved to customer facilities by transport tanker. There are between 86 and 98 product terminals across Canada. None of these terminals necessarily stores these fuels, and in particular the terminals in western Canada may store little or none. Maximum individual tank sizes at terminals are expected to be in the range of 20–30 million litres. No data were found documenting the number of terminals storing HFOs or their volumes (Cheminfo 2009).

Overall, the refinery production of Fuel Oil No. 4, Residual Fuel Oil and Fuel Oil No. 6 in 2008 appears to have decreased relative to 2004, based on production and movement statistics (Statistics Canada 2005–2009; Table C-1c in Appendix C). This is likely due to the increased use of other energy sources such as natural gas, and the reduced use of energy overall by users of HFOs (Statistics Canada 2007; Little et al. 2003).

5. Uses

Fuel Oil No. 6 (Bunker C) is used as a fuel at refineries, for electricity and steam generation by utilities and industry, and for other energy applications. Fuel Oil No. 6 is also used for water and space heating, pipeline pumping and gas compression, and is used with road oils (ATSDR 1995; Cheminfo 2009). Typically, Fuel Oil No. 6 needs to be heated to keep it flowable for use.

Residual Fuel Oil is similar to Fuel Oil No. 6 (albeit slightly lighter) and therefore is assumed to have similar uses. It may be used in furnaces and boilers of utility power plants, industrial power plants and metallurgical operations (Irwin et al. 1997).

Fuel Oil No. 4 is used in industrial plants and commercial burner installations that are not equipped with preheating facilities (Statistics Canada 2007), and is used in small to medium-sized ships as marine diesel fuel (like Diesel Fuel No. 4). In extremely cold weather, it does not need to be preheated for handling because its viscosity range allows it to be pumped and atomized at relatively low storage temperatures (CONCAWE 1998).

Usage of these three substances in Canada is variable, ranging from 6711 million litres in 2006 to 7567 million litres in 2007 to 6632 million litres in 2008 (Table C-1b in Appendix C). There was an overall usage decline in Ontario and an increase in Quebec and western Canada (Table C-1b in Appendix C). Almost 1100 million litres were added to inventories at utilities and within industry, which indicates that HFOs are stored in Canada (Statistics Canada 2010).

About 60% of the consumption of Fuel Oil No. 4, Residual Fuel Oil and Fuel Oil No. 6 (over 4200 million litres) is used for energy production (Statistics Canada 2010; Table C-2 in Appendix C). Utility companies in Atlantic Canada are the primary users of HFOs for thermal electric generation. In 2005, almost 15% of Atlantic Canada's electricity originated from this fuel source (Statistics Canada 2007). Quebec and Ontario also combust HFOs to generate electricity.

A detailed breakdown of the uses by industrial sector is shown in Table C-3 in Appendix C. In 2008, industrial sectors with the highest consumption of Fuel Oil

No. 4, Residual Fuel Oil and Fuel Oil No. 6 were the manufacturing, marine transportation and commercial/institutional sectors (about 89% of the total sector consumption). Most industrial sectors use the HFOs for power and heat generation.

Power generation for marine transportation is the only sector that observed an increase in HFO use from 1990 to 2005 (Statistics Canada 2007). In this industrial sector, HFOs represent 61% of fuel consumption; diesel represents 39% (Statistics Canada 2007). In 2005, more than 55% of HFO sales for the marine transportation sector were in British Columbia, followed by 23% in Quebec, 12% in Atlantic Canada and 10% in Ontario (Statistics Canada 2007).

Fuel Oil No. 4 has been classified as a List 2 formulant by Health Canada's Pest Management Regulatory Agency (PMRA 2010) and its use is subject to the regulatory directive on formulants (PMRA 2006).

6. Releases to the Environment

Fuel Oil No. 4, Fuel Oil No. 6 and Residual Fuel Oil may be released into the environment from activities in facilities associated with production, transportation and storage, as well as during refuelling and through commercial use.

Fuel Oil No. 4 and Fuel Oil No. 6 originate from distillation columns as a residual fraction (bottom product) or a distillate in a refinery or upgrader. Fuel Oil No. 4 and Residual Fuel Oil can also be blends of such residues with lighter distillates (IARC 1989a). Thus, the potential locations for the controlled release of Fuel Oil No. 4, Fuel Oil No. 6 and Residual Fuel Oil include relief valves and venting valves or drain valves on piping or equipment (e.g., vessels) in the vicinities surrounding this equipment. Under typical operating conditions, releases of HFOs would be captured in a closed system, according to defined procedures, and returned to the processing facility or to the wastewater treatment plant. In both cases, exposure of the general population or the environment is not expected.

Unintentional releases of Fuel Oil No. 4, Fuel Oil No. 6 and Residual Fuel Oil may occur at production facilities. Legislation affects releases of HFOs and includes requirements at the provincial/territorial level to prevent or manage the unintentional releases of petroleum substances and streams within a facility through the use of operating permits (SENES 2009). Such control measures include appropriate material selection during the design and set-up processes; regular inspection and maintenance of storage tanks, pipelines and other process equipment; the implementation of leak detection and repair or other equivalent programs; the use of floating roofs in above-ground storage tanks to

reduce the internal gaseous zone; and the minimal use of underground tanks, which can lead to undetected leaks or spills (SENES 2009).

At the federal level, unintentional releases of some petroleum substances to water from facilities are addressed by the *Petroleum Refinery Liquid Effluent Regulations* and guidelines under the *Fisheries Act* (Canada 2010). Additionally, existing occupational health and safety legislation specifies measures to reduce occupational exposures of employees, and some of these measures also serve to reduce unintentional releases (CanLII 2001). Non-regulatory measures (e.g., guidelines, best practices) are also in place at petroleum sector facilities to reduce unintentional releases. HFO evaporative emissions are not anticipated to comprise a large proportion of overall site emissions at production facilities. Thus, on-site releases are not expected to be a significant source of exposure.

Fuel Oil No. 4, Fuel Oil No. 6 and Residual Fuel Oil may be stored in bulk prior to transport to export wharves or to the marketplace. Potential exposure to releases from HFOs in bulk storage facilities is considered in the human health portion of this assessment. There is limited information on the production and transportation of Residual Fuel Oil. However, it is expected that Residual Fuel Oil is transported and stored in the same manner as Fuel Oil No. 4 and Fuel Oil No. 6 given its similar properties.

HFOs can be transported between facilities, as well as to the sectors identified in Table C-3 (Appendix C). Fuel Oil No. 4, Fuel Oil No. 6 and Residual Fuel Oil can be transported by pipeline, ship, rail and truck. In general, three operating procedures are involved in the process of transportation: loading, transit and unloading. Loading and unloading of HFOs is normally conducted at sites with limited access to the general public, such as bulk terminals and wharves.

The handling of Fuel Oil No. 4, Fuel Oil No. 6 and Residual Fuel Oil at petroleum facilities for the purpose of transportation is regulated at both the federal and provincial levels, with legislation covering loading and unloading (SENES 2009). Collectively, this legislation establishes requirements for the safe handling of petroleum substances and is intended to minimize or prevent potential releases during loading, transportation and unloading operations (SENES 2009). Releases of HFO vapours from the storage tanks into the air are expected to be small due to the low volatility of the substances.

Releases from washing or cleaning transportation vessels are not considered in this screening assessment, as tanks or containers for transferring petroleum substances are typically dedicated vessels; washing or cleaning, therefore, is not required on a routine basis (U.S. EPA 2008). Cleaning facilities require processing of grey water to meet local and provincial release standards.

6.1 Release Estimation

Fuel Oil No. 6 is approved for use in Nunavut as a dust suppressant (Government of Nunavut 2002). However, there is no indication that it is being used in Nunavut for this purpose, and it is considered unlikely that a fuel would be used due to the high cost of fuels in the Arctic (personal communication, telephone discussion between Environmental Protection, Nunavut Department of Environment and Ecological Assessment Division, Environment Canada, November 20, 2013; unreferenced). Therefore, this release scenario is not considered further in this assessment.

HFOs are transported by pipeline, ship, barge or rail to refined product terminals. The oil is then moved by tanker truck to storage facilities (Statistics Canada 2007). Thus, HFOs can be stored in large storage tanks that range in size from 20 to 1000 megalitres (Cheminfo 2009). Storage tanks can be located above ground, in ground or, in the case of smaller-scale storage, indoors in basements or garages. With the transport of these substances by ship, train, pipeline or truck, unintentional releases of HFOs will generally enter the air, water or soil depending on the modes of transportation involved.

Unintentional spills or leaks during the handling and transit processes were considered in this screening assessment for the potential to cause ecological harm. Due to the low volatility of these HFOs as defined by their physical-chemical properties, evaporative emissions into the air from unintentional spills would occur in a lower proportion compared to the proportions entering water or soil.

Potential releases associated with the transport of these HFOs were assessed through analysis of historical spill data (2000–2009) from Environment Canada's National Enforcement Management Information System and Intelligence System (NEMISIS) database (Environment Canada 2011a). NEMISIS provides national data on releases of substances involving or affecting a federal agency or department, a federal government facility or undertaking, or Aboriginal land; or releases that contravene CEPA 1999 or the *Fisheries Act*; releases that affect fish, migratory birds or species at risk or that impact an interprovincial or international boundary; and releases from marine vessels. Other spills may be reported to NEMISIS, but there is no legal requirement to do so. In addition, spills data provided to NEMISIS may vary depending on the provincial reporting requirements, such as spill quantity reporting thresholds.

The majority of the data reported were labelled as Bunker C. There were some releases that were generically labelled as Bunker with no indication as to what specific type of Bunker was released. It is not known if spills of Fuel Oil No. 4 or Residual Fuel Oil would be reported as either generic Bunker or Bunker C. Thus, all releases reported as either Bunker or Bunker C were considered in this assessment to represent all three substances (Fuel Oil No. 4, Fuel Oil No. 6 and

Residual Fuel Oil), although there is a possibility that this spills information captures other HFOs. Extremely large spills of suspicious origin were investigated to ensure that they were not from environmental emergencies training exercises. One spill from the NEMISIS database that was not included in the analysis of spills in this report was a release in 2005 of 734 000 L of Bunker C in Alberta, as it was an unusually high release. While there is the inherent possibility that a similar catastrophic spill could occur, a spill of that magnitude has occurred only once in a span of 10 years (2000–2009) in Canada. Not included in the release estimate are spills where collisions, poor road conditions or adverse weather-related events are listed as a reason for, or source or cause of, the spill.

Many of the reports had no estimate of the volume released into the environment. To account for the underestimation of the total volume released, the estimated total annual volumes were extrapolated by assuming that the distribution of reported volumes released were representative of all releases. Results are shown in Table C-4 (Appendix C). From 2000 to 2009, the total extrapolated volume spilled of Fuel Oil No. 6 (Bunker C) to all media (soil, saltwater and freshwater) was 2.4 million litres from 339 spills. The average spill volume (2000–2009) was 7072 L (total extrapolated volume spilled/reported number of spills).

From 2000–2004, there was a gradual increase in the total volume of Fuel Oil No. 6 spilled (Table C-4 in Appendix C). This trend, however, may be due to the increased reporting of spills. Quebec had the highest total volume of Bunker C spills, followed by Nova Scotia. Release volumes by year for each province are displayed in Table C-5 (Appendix C).

The NEMISIS database also separates spill data into the specific compartment affected (air, land, freshwater, saltwater), so that the estimated average release quantity per spill to each compartment can be determined (Table C-6 in Appendix C). From 2000 to 2009, there were 131 spills to land, 55 spills to freshwater and 108 spills to marine water (Table C-6 in Appendix C). The total number of spills listed in Table C-6 (Appendix C) does not equate to the total shown in Table C-4 (Appendix C), because some spills affected more than one compartment, while others had no listed compartment affected in the NEMISIS database (Environment Canada 2011a).

Within each compartment, a similar extrapolation was conducted to account for reported spills with no associated volumes. The estimated average release quantities per spill of these HFOs to freshwater, saltwater and soil are shown in Table 6-1. These values were used for determining the predicted environmental concentration (PEC) in the ecological exposure assessment. In Table 6-1 there is no distinction in the database as to whether the spills occurred during loading, transport or unloading. Thus, the average spill volume was used for each of the scenarios.

Table 6-1. Estimated average release quantities per spill of Fuel Oil No. 4, Residual Fuel Oil and Fuel Oil No. 6 to various compartments (L/spill) based on historical spill data from 2000 to 2009 from Environment Canada (2011a)[a]

Compartment affected	Average releases due to spills, kg per spill[b]	Average releases due to spills, L per spill[c]
Freshwater[d]	14 790	15 090[b]
Saltwater	12 860	13 120
Soil	4810	4910

[a] Does not include releases due to aircraft crash, collision, ice/frost, road conditions, subsidence or vandalism.
[b] Determined based on an average density of 0.98 kg/L (Environment Canada c2001).
[c] Average release (litres) of these HFOs to each compartment was determined by separating all releases labelled as either Bunker or Bunker C from 2000 to 2009 into specific compartments (marine, freshwater, soil), determining the extrapolated total released within each compartment and then dividing this extrapolated total by the total number of spills affecting that compartment.
[d] Does not include the 2005 Lake Wabamun spill (734 000 L).

In the case of ship loading, transport and unloading, an average of 13 120 L per spill is expected in marine water, while 15 090 L per spill is expected in freshwater. The same historical data indicate that, in Canada from 2000–2009, the average spill to soil was 4910 L.

The NEMISIS database also provides three columns of data (sources, causes and reasons) for many of the releases of Bunker C. The data in these columns were analyzed to determine how and why the majority of Bunker C releases occur (Table C-7a – C-7c in Appendix C).

The largest spill of Fuel Oil No. 6 (Bunker C) in Canada occurred in 2005 near Lake Wabamun, Alberta and was a result of a train derailment, releasing 734 000 L of Bunker C into the water. Removal of this spill from the analysis shifted the volume-based analysis of major sources, causes and reasons for Bunker C spills in Canada. The industrial areas where the majority of Bunker C releases occur (Table C-7a in Appendix C) are other watercraft (25% of volume), pipelines (20% of volume) and marine tankers (19% of volume). Tank trucks, transport trucks and other motor vehicles only account for 2% of the volume spilled. Thus, truck transport is not considered a significant source of Bunker C spills. Notably, removal of the 2005 Lake Wabamun train derailment reduces the proportion spilled during train transport from 33% to 2%, and the majority of this release was from one incident of 60 000 L.

The NEMISIS data were also analyzed for causes of HFO leaks (Table C-7b in Appendix C). It was found that pipe leaks accounted for 38% of the volume released, which is consistent with pipelines as a major source of Bunker C releases (Table C-7a in Appendix C). Likewise, the sinking and grounding of

vessels accounted for 13% and 6% of the total volume, respectively, which is also consistent with the high total spill volume by watercraft as a source. Some 8% of the volume spilled was due to unknown causes.

Table C-7c (Appendix C) identified that a large proportion of spills (43% by volume) were due to unknown reasons. Material failure accounted for 16% and human error accounted for 16%. The remaining 25% were due to a wide variety of reasons.

Based on an analysis of the available data, there were relatively few spills to land as a result of truck transport (32 spills) and even fewer by train transport (11 spills) over this 10-year period (Environment Canada 2011a).

7. Environmental Fate

When petroleum products are released into the environment, four major fate processes will take place: dissolution in water, volatilization, biodegradation and adsorption. These processes will cause changes in the composition of these UVCB substances. In the case of spills on land or water surfaces, photodegradation—another fate process—can also be significant.

As noted previously, the solubility and vapour pressure of components within mixtures will differ from those of the component alone. These interactions are complex for complex UVCBs such as petroleum hydrocarbons.

Each of the fate processes affects hydrocarbon families differently. Aromatics tend to be more water-soluble than aliphatics of the same carbon number, whereas aliphatics tend to be more volatile (Potter and Simmons 1998). Thus, when a petroleum mixture is released into the environment, the principal water contaminants are likely to be aromatics, whereas aliphatics will be the principal air contaminants (Potter and Simmons 1998). The trend in volatility by component class is as follows: alkenes ≈ alkanes > aromatics ≈ cycloalkanes. The most soluble and volatile components have the lowest molecular weight; thus, there is a general shift to higher molecular weight components in residual materials.

When Fuel Oil No. 6 is spilled, only 5–10% is expected to evaporate in the first hours following the spill (NOAA 2010; Environment Canada 1999; API 2004). The rates of evaporative emission of a given HFO are proportional to the percentage of volatile components (Smith and MacIntyre 1971). Following an initial loss due to volatilization and solubilization, the remaining degradative pathway is biodegradation, usually by bacteria.

Biodegradation is almost always operative when petroleum mixtures are released into the environment. It has been widely demonstrated that nearly all soils and

sediments have populations of bacteria and other organisms capable of degrading petroleum hydrocarbons (Pancirov and Brown 1975). Degradation occurs both in the presence and absence of oxygen. Two key factors that determine degradation rates are oxygen supply and molecular structure. In general, degradation is more rapid under aerobic conditions. Decreasing trends in degradation rates according to structure are as follows (Potter and Simmons 1998):

(1) *n*-alkanes, especially in the C_{10}–C_{25} range, which are degraded readily;
(2) isoalkanes;
(3) alkenes;
(4) benzene, toluene, ethylbenzene, xylenes (BTEX) (when present in concentrations that are not toxic to microorganisms);
(5) monoaromatics;
(6) polynuclear (polycyclic) aromatic hydrocarbons (PAHs); and
(7) higher molecular weight cycloalkanes (which may be very slow to degrade (Pancirov and Brown 1975)).

Three weathering processes—dissolution in water, volatilization and biodegradation—typically result in the depletion of the more readily soluble, volatile and degradable compounds and the accumulation of those most resistant to these processes in residues.

7.1 Experimental Studies

Within the first year following a spill to water, it is expected that there will be the complete removal of *n*-alkanes up to C_{17} (Kolpack et al. 1978; Guard and Corbet 1972). The remaining lower molecular weight fraction would be expected to disperse into the water column (API 2004). Tables D-1 and D-2 (Appendix D) provide changes to the chemical characterization of Fuel Oil No. 6 after 2.5% weathering. There is the initial removal of light saturates due to evaporation, and of low molecular weight aromatics, likely due to dissolution (tables D-1 and D-2 in Appendix D).

The behaviour of spilled HFOs in water has also been observed in past spill incidences, such as the 2005 train derailment that released 730 000 L of Fuel Oil No. 6 near Lake Wabamun, Alberta. Within hours of the spill, submerged tar balls were observed in the nearshore regions and were seen riding up and down in the water column (Fingas et al. 2006). This neutrally buoyant behaviour of spilled HFOs was due to the product's density—close to that of freshwater—combined with evaporation, temperature changes, uptake of solid matter and photo-oxidation (Fingas et al. 2006). When HFOs are warmed by the sun, they become more viscous due to the evaporation of the low molecular weight aliphatics and dissolution of their low molecular weight aromatics. The heavy fraction that remains tends to sink due to its high density and it can be further

weighted down by entrained sand (Fremling 1981). The oil, however, can resurface due to the loss of solid matter, uptake of lighter material (e.g., dry grass, insects, etc.) and changes in temperature or salinity (Fingas et al. 2006).

Only a small proportion of Fuel Oil No. 6 is biodegradable. Its high molecular weight and hydrocarbon complexity decreases its susceptibility to biodegradation (Foght 2006; Walker et al. 1976). Walker et al. (1976) found that 11% (by weight) of Fuel Oil No. 6 was biodegraded over 28 days when incubated with a mixed culture of estuarine bacteria in a nutrient medium. There was 10% degradation of the aromatic fraction and 25% degradation of saturates (Walker et al. 1976). This is supported in the field, as biodegradation of Fuel Oil No. 6 spilled in Lake Wabamun accounted for the loss of 12% by weight of the oil added to bacterial cultures (Foght 2006). Thus, Fuel Oil No. 6 has a small proportion of biodegradable low molecular weight hydrocarbons (saturates and small aromatics) and a large proportion of components that are not readily biodegradable (complex aromatics, resins, asphaltenes) (Foght 2006; Zajic et al. 1974). Heavier PAHs with increased alkylation also decrease biodegradation efficiency (Diez et al. 2005).

The formation of tar balls also limits microbial access to the biodegradable components of spilled Fuel Oil No. 6 (Foght 2006). As well, the rate of biodegradation in water also depends on the coastal environment.

Much about the environmental fate of Fuel Oil No. 6 (Bunker C) can be learned from previous spill incidents, principally from the 1970 *Arrow* spill, in which Bunker C presence was monitored for decades after the initial spill of 9000 tonnes, as discussed below. Experimental fate data for the other two CAS RNs were not available. However, considering the similar, albeit lighter, composition and physical-chemical properties of Fuel Oil No. 4 and Residual Fuel Oil to Bunker C, we can assume that the experimental data would apply to these two substances.

Three years after the *Arrow* spill, an estimated 3.5% of the Bunker C remained (Owens et al. 1994a, 1994b). The stranded oil residues mixed with sediment and had surface-weathered to form a hard crust (asphalt pavements), and some oil was buried by sediment from the intertidal zone by wave action (Owens 1978).

Three and a half years after the *Arrow* spill, Bunker C in high-energy conditions (oiled beach that was directly exposed to considerable wave action) had significantly changed from its original composition (Rashid 1974). Saturated and aromatic hydrocarbons were reduced to 34% of the composition compared to 51% in reference HFO samples that were placed in capped storage. There was also an increase in the non-hydrocarbon fraction from 49 to 66% (Rashid 1974). By comparison, samples in low to moderate energy coasts (little or no wave action) had relatively slower degradation rates that were only slightly more than the reference samples (Rashid 1974).

Five years following the *Arrow* spill, Fuel Oil No. 6 was still present, ranging from an iridescent sheen to 203-cm-thick tar deposits. In high-energy locations, oil was found under boulders, while in low-energy beaches the tar was contained in sediment and stranded kelp (Vandermeulen and Gordon 1976). The stranded oil tended to re-enter the littoral and sublittoral areas, although little entered the water column directly (Vandermeulen and Gordon 1976). Sediment-bound tar appeared to be altered by microbial activity and dissolution, with the removal of most *n*-alkanes below C_{28}. Seven years after the *Arrow* spill, Fuel Oil No. 6 was still found in the subsurface sediments and on some shorelines (CONCAWE 1998). After 22 years, 0.5% of the oil remained, of which 10% was heavy and 70% was light (Owens et al. 1994a, 1994b).

Oil from the *Arrow* was still present 30 years after the spill, primarily in sheltered areas such as low-energy lagoons (Lee et al. 2003). Vandermeulen and Gordon (1976) acknowledge that oil residues that have not been attenuated within 5 years have the potential to remain for long periods of time. Based on flow experiments, Vandermeulen and Gordon (1976) suggest that stranded oil can remain for longer than 150 years, although this may be an underestimate, as they assumed a linear removal rate. Vandermeulen (1977) suggests that the erosion half-life for total sediment-bound Fuel Oil No. 6 is in excess of 25 years and possibly longer.

Biodegradation of Fuel Oil No. 6 has been shown to occur at temperatures as low as 5°C (Mulkins-Phillips and Stewart 1974), although less readily than at higher temperatures. Temperature may limit the rate of natural biodegradation of oil in marine temperate-to-polar zones: the decreased temperature resulted in extended lag phases of the growth curve of *Nocardia* sp. and the Fuel Oil No. 6 degradation curve (Mulkins-Phillips and Stewart 1974). Thus, in arctic regions, it takes longer for oil to biodegrade (Mulkins-Phillips and Stewart 1974).

7.2 Fate Estimated from Physical-chemical Properties

Due to the complex interaction of components within a mixture that impacts their physical-chemical properties and behaviour, it is difficult to predict the fate of a complex mixture. Therefore, as a general indication of the fate of HFOs, the physical-chemical properties of representative structures of HFOs (Table B-1 in Appendix B) were examined.

Based on the physical-chemical properties of representative structures of HFOs, the majority of components are expected to partition to water and soil.

C_{12}–C_{50} components have boiling points from 155 to 722°C. The individual components of HFOs are characterized by low to moderate water solubilities (5×10^{-21} to 3.9 mg/L), low vapour pressures (1.2×10^{-18} to 165 Pa), low to high Henry's Law constants (0.03 to 2×10^{11} Pa·m^3/mol), moderate to high log K_{ow} values (3.9 to 25), and moderate to high log K_{oc} values (3.6 to 21.2) (Table B-1 in Appendix B).

If released to air, the lower molecular weight alkanes and aromatic hydrocarbons will mainly partition to air (European Commission c2000a). With increasing molecular weight, these components will preferentially partition to soil and sediment (European Commission c2000a). However, based on low vapour pressures (1.2×10^{-18} to 165 Pa), the majority of components of HFOs are not expected to remain in air (Table B-1 in Appendix B). Therefore, releases of HFOs to air are unlikely.

The density of Fuel Oil No. 6 is close to that of water (0.94 to 1.01 g/mL; CONCAWE 1998, Environment Canada c2001). Thus, upon entering water, some components are expected to rise to the surface and spread out while others will remain suspended in the water column. Based on the water solubility of these components (5×10^{-21} to 3.9 mg/L), if a release occurs to water, smaller components (< C_{20}) will dissolve in water. The larger > C_{20} components are not expected to dissolve into water. HFOs are expected to sorb to suspended solids and sediments based upon their moderate to high estimated log K_{oc} values (Table B-1 in Appendix B).

The loss of the lower-weight components due to evaporation and dissolution will result in a density increase of the residual, thereby sinking its remaining components (Irwin et al. 1997; CONCAWE 1998). The tar-like consistency of the resulting HFO will increase its absorption to particulates, and thus HFOs are expected to have a large proportion of the mixture partitioning to sediment (CONCAWE 1998). It is likely that, with a release situation into water where the HFO is not immediately in contact with sediments or suspended matter, the moderate to high Henry's Law constants will drive the C_{12}–C_{20} components out of the water. The tendencies for evaporation and sorption compete, so that the exact nature of the release would dictate how the HFO behaves.

If released to soil, all components of HFOs are expected to have high adsorptivity to soil. Competing with this tendency are evaporative forces. Volatilization from moist soil surfaces may be an important fate process based upon estimated Henry's Law constant values of 0.03 to 2×10^{11} Pa·m^3/mol. Lower molecular weight representative structures of HFOs (alkanes, isoalkanes, cycloalkanes and one-ring aromatics) may slightly to substantially volatilize from dry soil surfaces based upon their moderate vapour pressures (Table B-1 in Appendix B).

When large quantities of a hydrocarbon mixture enter the soil compartment, soil organic matter and other sorption sites in soil are fully saturated and the

hydrocarbons will begin to form a separate phase (a non-aqueous phase liquid or NAPL) in the soil. At concentrations below the retention capacity for the hydrocarbon in the soil, the NAPL will be immobile (Arthurs et al. 1995).

8. Persistence and Bioaccumulation Potential

Due to the complex nature of petroleum substances such as HFOs, the persistence and bioaccumulation potential of components of these substances is characterized based on empirical and/or modelled data for a suite of petroleum hydrocarbons structures.

8.1 Environmental Persistence

Persistence was characterized based on empirical and/or modelled data for a suite of petroleum hydrocarbons expected to occur in petroleum substances.

Model results and the weighing of information are reported in the petroleum substances persistence and bioaccumulation supporting documentation (Environment Canada 2014). These data are summarized in Table E-1 in Appendix E.

Empirical and modelled half-lives in the atmosphere for many components of these HFOs are less than 2 days (Environment Canada 2014). However, some components, such as the C_{13} cycloalkane diaromatics, can have half-lives greater than 2 days, and may undergo long-range transport. In addition, a number of three- to six-ring PAHs can undergo long-range transport to remote regions due to sorption to particulate matter (Environment Canada 2014).

Considering biodegradation in water, soil and sediment, the following components are expected to have half-lives greater than 6 months in water and soils and greater than a year in sediments: C_{30} isoalkanes, C_{50} one-ring cycloalkanes, C_{15}–C_{50} two-ring cycloalkanes, C_{18}–C_{22} polycycloalkanes, C_{12} one-ring aromatics, C_{12}-C_{20} cycloalkane monoaromatics, C_{12}–C_{50} two-ring aromatics, C_{12} cycloalkane diaromatics, and C_{14}, and C_{30}–C_{50} three-ring aromatics, C_{16}–C_{20} four-ring aromatics, C_{20}–C_{30} five-ring aromatics and C_{22} six-ring aromatics. The C_{30} one-ring cycloalkanes, C_{12} dicycloalkanes, C_{14} polycycloalkanes, and C_{15} and C_{30}–C_{50} one-ring aromatics have half-lives greater than a year in sediments (Table E-1 in Appendix E).

8.2 Potential for Bioaccumulation

Bioaccumulation potential was characterized based on empirical and/or modelled data for a suite of petroleum hydrocarbons expected to occur in petroleum substances. Bioaccumulation factors (BAFs) are the preferred metric for assessing the bioaccumulation potential of substances, as the bioconcentration factor (BCF) may not adequately account for the bioaccumulation potential of substances via the diet, which predominates for substances with log K_{ow} > ~4.5 (Arnot and Gobas 2003).

In addition to fish BCF and BAF data, bioaccumulation data for aquatic invertebrate species were also considered. Biota-sediment/soil accumulation factors (BSAF), trophic magnification factors, and biomagnification factors were also considered in characterizing bioaccumulation potential.

Empirical and modelled bioaccumulation data for petroleum hydrocarbons, as well as the weighing of information, can be found in the supporting document for this assessment (Environment Canada 2014). A summary of the results for bioaccumulation potential is presented below and in Table E-2 in Appendix E.

Overall, there is consistent empirical and predicted evidence to suggest that the following components have the potential for high bioaccumulation with BAF/BCF values greater than 5000: C_{13}–C_{15} isoalkanes, C_{12}–C_{15} one-ring cycloalkanes, C_{12} and C_{15} two-ring cycloalkanes, C_{14} and C_{22} polycycloalkanes, C_{15} one-ring aromatics, C_{15}–C_{20} cycloalkane monoaromatics, C_{12}–C_{13} diaromatics, C_{20} cycloalkane diaromatics, C_{14} and C_{20} three-ring aromatics, C_{16}–C_{20} four-ring PAHs, C_{20}–C_{22} five-ring PAHs, and C_{22} six-ring PAHs (Table E-2, Appendix E). These components are associated with a slow rate of metabolism and are highly lipophilic. Exposures from water and diet, when combined, suggest that the rate of uptake would exceed the total elimination rate. Most of these components are not expected to biomagnify in aquatic or terrestrial foodwebs, largely because a combination of metabolism, low dietary assimilation efficiency and growth dilution allows the elimination rate to exceed the uptake rate from the diet (Environment Canada 2014); however, one study (Harris et al. 2011) suggests that some alkyl-PAHs may biomagnify. While only BSAFs were found for some PAHs, it is possible that BSAFs will be > 1 for invertebrates, given that they do not have the same metabolic competency as fish, but BSAFs will likely decrease beyond C_{22} due to reduced bioavailability of the higher boiling point fractions (Muijs and Jonker 2010).

9. Potential to Cause Ecological Harm

9.1 Ecological Effects Assessment

The toxicity of an HFO depends on the toxicity of the individual stocks from which it is blended (CONCAWE 1998). Toxicity data for Fuel Oil No. 4 were not available, and therefore only toxicity data for Fuel Oil No. 6 and Residual Fuel Oil are presented. Based on similarities in carbon and boiling point ranges between all three HFOs, we can expect similar toxicity for Fuel Oil No. 4.

9.1.1 Aquatic compartment

Experimental aquatic toxicity data (fish, invertebrates and algae) on Fuel Oil No. 6 and Residual Fuel Oil are detailed in tables F-1a and b (Appendix F).

Moderate toxicity (median lethal concentrations [LC_{50}] of 1.9–4.7 mg/L) was seen with the water-soluble fractions (WSFs) of Fuel Oil No. 6 in various fish species, including sheepshead minnows (*Cyprinodon variegatus)*, inland silverside (*Menidia beryllina)* and longnose killifish (*Fundulus similis)* (Table F-1a in Appendix F). Invertebrates were more sensitive than fish and algae to Fuel Oil No. 6, with LC_{50} values ranging from 0.9 to 6.3 mg/L (WSF) (Table F-1a in Appendix F; Saco-Alvarez et al. 2008). It is likely that the two- and three-ring PAHs and alkylated naphthalenes are largely responsible for the toxicity seen in these tests, as Fuel Oil No. 6 is composed of more of these compounds in comparison to other petroleum products that were found to be less toxic (Rossi et al. 1976; Rossi and Neff 1978; Tatem et al. 1978). Algae appear to be the least sensitive to Fuel Oil No. 6 in water, as median effective concentrations (EC_{50}) ranged from 160 to > 5000 mg/L. Likewise, treatment of algae (*S. capricornutum* and *M. aeruginosa*) at 100% WSF led to no inhibition in growth (Giddings et al. 1980). Available experimental aquatic toxicity data on light and heavy Residual Fuel Oil (CAS RN 68476-33-5) in *Oncorhynchus mykiss* (rainbow trout) and *Daphnia magna* (water flea) in Table F-1b (Appendix F) show relatively low toxicity (100–1000 mg/L) for loading rates. Likewise, there was low relative toxicity (30–300 mg/L) to the algae *Raphidocelis subcapitata* (Table F-1b in Appendix F).

Strobel and Brenowitz (1981) found that Fuel Oil No. 6 is toxic to juvenile horseshoe crabs (*Limulus polyphemus*). After exposure to 2.25 mg/L of Fuel Oil No. 6 for 7 days, there was a significant increase in mortality relative to the control, with 26% dead compared to 16% dead in the controls. The major effect of the HFO was the delay of moulting (development), and it had a positive linear relationship with the oil concentration. These developmental effects suggest that HFO contamination may have long-term effects on horsehoe crab populations by decreasing the size of an age class and affecting future adult fecundity.

Following the *Arrow* spill of Fuel Oil No. 6 off the coast of Nova Scotia, there were significant short-term mortalities of soft-shell clams (*Mya arenaria*) (Thomas 1973). Mortality rates were related to the oil cover. Total mortalities ranged from 15.8% with 1.7% oil cover, to 70.3% with 96.7% oil cover (Thomas 1973). In

areas with the greatest oiling, clams were observed to vacate their burrows, which exposed them to their predators. Gilfillan and Vandermeulen (1978) determined that oiled areas following the *Arrow* spill resulted in the reduction in population growth of soft-shell clams (*Mya arenaria).* Oiled sediments had concentrations of oil up to 3800 µg/g, and clams had oil concentrations of up to 200 µg/g hydrocarbon in their tissues. In the non-oiled population, there were greater numbers of clams per square metre and a higher proportion of older clams, based on age. In comparison, the oiled population had very equal numbers of older and younger individuals. Growth in the oiled population decreased by greater than 60%, compared to populations in the non-oiled lagoon, which decreased by 40.9% (Gilfillan and Vandermeulen 1978). Oiled clams have been shown to gain carbon at slower rates than those not exposed to oil, and are thus less efficient at utilizing food (Gilfillan et al. 1976; Vandermeulen 1977; Gilfillan and Vandermeulen 1978). Gilfillan et al. (1976) found that *M. arenaria* in oiled conditions were growing 50% less than populations in non-oiled areas. Six years after the *Arrow* spill, there were reduced numbers of clams and lower growth rates (Gilfillan and Vandermeulen 1978). Nine years after the spill, the growth of these clams was still retarded (MacDonald and Thomas 1982). Direct observations and a survey 30 years after the spill found an abundance of *M. arenaria*, suggesting habitat recovery (Lee et al. 2003).

It appears that coral species can survive short exposures (5–30 minutes) of Bunker C (Reimer 1975). A longer exposure time of 13 days reduces the amount of live tissue, and after 16 days there can be almost no tissue remaining (Reimer 1975). Species that secrete mucus appear to be protected from oil, thereby reducing the impact of the oil (CONCAWE 1998; Reimer 1975; Wicksten 1984). The mucus-covered tissues of sea anemones appear to repel oil, as they can withstand submersion in Bunker C for up to 1 hour without visible adverse effects (Wicksten 1984).

HFOs are also harmful to aquatic organisms through contact with eggs. DeBruyn et al. (2007, 2008) compared the pattern, frequency and severity of deformity in larvae of lake whitefish (*Coregonus clupeaformis*) and northern pike (*Esox lucius*) as a result of PAH exposure from areas affected by the Lake Wabamun Fuel Oil No. 6 spill relative to background PAH levels. All sites in the lake showed incidences of deformity that were higher than what is typically observed in laboratory studies (deBruyn et al. 2007, 2008). The three lake whitefish egg incubation trays with the highest PAH exposure (oil-based) had a 5–15% higher frequency of moderate-to-severe skeletal, craniofacial and finfold deformities, although larval growth and egg survival were not affected. Hatching success at the oil exposed condition was 29 ± 16%, while the reference site hatching success was 38 ± 16%. In comparison, northern pike had no oil-related effects on development (deBruyn et al. 2008). In fact, hatching success was higher in the oil-exposed areas than in reference areas. Thus, northern pike appears to be more tolerant to PAH exposure or has a lower uptake of PAHs than lake whitefish.

As previously mentioned, weathered tar balls tend to sink to the lake/ocean floor. Fremling (1981) believed that sunken oil can add critical stress to spawning bluegills (*Lepomis macrochirus*). Bluegills, which scour lake bottoms for nests when they spawn, were likely in contact with sunken oil that may have irritated their pharyngeal areas and led to a bacterial infection (Brown 1980; Fremling 1981). In the case of the 28 000-L spill of Fuel Oil No. 6 in Lake Winona, 190 000 bluegills died (Fremling 1981).

Other observed mortality and deformation in fish include effects on eggs of cod (*Gadus morhua*) and pollock (*G. virens*) following the *Argo Merchant* spill of Bunker C in 1976 (Longwell 1977).

Mussels (*Mytilus galloprovincialis*) along the Galician and Bay of Biscay coast were studied from 2003–2006 after the release of Bunker C from the *Prestige* oil tanker to determine what, if any, changes had occurred in their reproductive parameters (Ortiz-Zarragoitia et al. 2011). In April 2003, female mussels showed a high prevalence of oocyte atresia, which may decrease gamete quality. Hemocytic infiltration of the follicles was also observed in both sexes. In April 2004, no atresia was found, but both male and female mussels had reduced follicle size. The effect of reduced follicle size on mussel reproductive ability is unknown. In April 2006, female mussels from certain sites had necrotic gametes.

In comparison, toxicity tests with water-soluble extracts of Fuel Oil No. 6 have little negative impact on the fertilization of sea urchin eggs (Allen 1971). They were only found to be toxic to fertilization at 50% or greater oil saturation (Allen 1971). However, the HFO did have a noticeable effect on cleavage (division of cells in the early embryo) and development, as it was found to be toxic at 6.25% or greater oil saturation (Allen 1971). Fuel Oil No. 6 was found to have the most inhibiting effect on egg cleavage in comparison to other highly refined petroleum products (Allen 1971). This suggests that refining removes the more toxic fractions, likely through evaporation (Allen 1971).

The critical toxicity value (CTV) selected for the freshwater exposure scenarios for ship loading/unloading and transport was the lowest available experimental value, which was the 48-hour acute EC_{50} (immobilization) of 4.1 mg/L in *Daphnia magna* (MacLean and Doe 1989; Table F-1a in Appendix F). Fluorescence spectroscopy was the analytical method used in this study for determining concentrations; this method measures the concentration of aromatics, not total petroleum hydrocarbons, and thus the CTV can be considered conservative. The CTV used for saltwater exposure scenarios was the 48-hour acute LC_{50} of 0.9 mg/L in *Mysidopsis almyra* for both ship loading/unloading and transport (Anderson et al. 1974; Table F-1a in Appendix F). This study is considered acceptable.

9.1.2 Avian toxicity

HFOs can have a wide variety of effects on birds, especially sea birds. The toxic effects of Bunker C on seabirds have been well documented due to historical and ongoing oil spills. The immediate effect of HFOs in water is most often mortality due to the adherence of oil to the plumage. Even small amounts of oil compromise the integrity of the waterproofing and insulation provided by feathers (Leighton 1993). Reduced buoyancy may cause a bird to sink and drown, while the lack of insulation causes seabirds to either die from hypothermia or increase their metabolic activity to the point where they die from starvation or exhaustion (Clark 1984; Hartung 1995; Leighton 1993).

Wiese and Robertson (2004) estimated that approximately 300 000 seabirds die annually in the waters south and east of Newfoundland and Labrador due to chronic oil pollution, although these releases occur well offshore. The waters of the Grand Banks are used as wintering areas for millions of seabirds; many are thick-billed murres (*Uria lomvia*), common murres (*U. aalgae*) and dovekies (*Alle alle*). Most of the birds that are contaminated are exposed to HFOs (Bunker C) and lubricants from passing ships. The immediate effects are from physical contamination of feathers, hypothermia and excessive resorption of fat stores. Birds that are affected the most by oil spills are those that spend most of their time on water and dive rather than flying up when disturbed (Clark 1984). Likewise, bird species dependent on feeding in water, such as diving birds, are more susceptible to oiling than semi-aquatic birds that can feed elsewhere.

Nesting birds that come into contact with HFOs may transfer oil from their feathers and feet to their eggs during incubation. Toxicity to eggs via this route has been shown (Michigan 2010). It also appears that seabirds, including murres (which are common in Canada), are highly aggregated off southwest Vancouver Island and have highly clumped distributions (Burger 1993a). This suggests a greater impact, should the aggregates be near the source of an HFO spill.

In 1976, a spill of 1.2 million litres of Fuel Oil No. 6 into the St. Lawrence River resulted in the death of 225 birds, including great blue herons, Canada geese and other various bird species (Smith 1976). In 1988, the *Nestucca* spill of 875 000 L of Fuel Oil No. 6 from a barge resulted in the oiling of at least 30 000 murres and Cassin's auklets (*Ptychoramphus aleuticus*), along with the death of 56 000 seabirds (Ford et al. 1991; Burger 1993b). Most of the dead birds were encapsulated in a thick oily mousse, and 75% had over 95% of their plumage saturated in oil. Following the Fuel Oil No. 6 spill in Lake Wabamun in 2005, 530 oiled birds were recovered within 5 days, although 156 were already found dead upon arrival at the recovery centre (TSB 2005). Of those that were recovered after the Lake Wabamun spill, Patterson and Pimblett (2007) suggest that the recovery of birds after oiling has a success rate of only 25%.

Shorebirds ingest about 50% of the crude oil on their plumage (through preening) within 8 hours of oil exposure (Hartung and Hunt 1967). This percentage of

ingestion is likely similar for the ingestion of HFOs. Thus, moderately oiled ducks with an average of 7 g of oil on their feathers will ingest approximately 3.5 g of oil over an 8-day period (0.437 g/day) (Hartung and Hunt 1967). Oral dosing is an important exposure route for birds such as mallards, because their metabolic rates are not significantly altered by oil adherence (Peakall et al. 1982). Only some of the ingested oil is actually absorbed, as glaucous-winged gulls (*Larus glaucenscens*) excreted 36 ± 20% of a 500 mg oral dose of Bunker C (McEwan and Whitehead 1980).

The ingestion of HFOs is expected to have a negative effect on egg hatching success at high doses. Ainley et al. (1981) fed auklets capsules of 9, 300 or 600 mg of Fuel Oil No. 6 and did not find any significant differences from the controls. At a higher oral dose of 1000 mg, there was a significant drop in eggs laid, with 82.9% laid, compared to 91.7–94.9% laid in the controls. For hatching, there was a significant drop at oral doses of 600 mg and 1000 mg Fuel Oil No. 6, with a 68.6–69% hatching success compared to controls (82.7–85.7% hatching success). The period of 9–13 days after dosing was considered the critical time for auklets, as fed auklets retained oil approximately 3 hours longer than quail, thereby extending the exposure time and possibly increasing the toxicity of oil to auklet and the forming egg (Ainley et al. 1978, 1981).

The external application of Fuel Oil No. 6 on eggs has also been shown to reduce hatching success and survival. Application of 5, 10, 20 and 50 µL of Fuel Oil No. 6 externally to sets of mallard eggs (*Anas platyrhynchos*) resulted in reduced hatchability (Szaro 1979). An applied dose as small as 5 µL of Fuel Oil No. 6 led to a significant reduction in 30-day hatching success to 36%, while 6-day survival decreased to 52% compared to 100% in the controls (Szaro 1979). Similarly, Grau et al. (1977) found that Fuel Oil No. 6 on quail eggs was toxic to embryos after the application of 50–100 µL to the plumage of adult quail. This indirect contamination of quail eggs resulted in reduced egg production and egg viability (Grau et al. 1977). Wootton et al. (1979) also determined that a petroleum ether extract dose of 300 mg of Venezuelan Bunker C reduced production and hatchability to virtually zero after one day.

Considering the small amounts of HFOs required to affect the eggs of birds and the numbers of oiled seabirds that are found along Newfoundland beaches, it is expected that a chronic loss of eggs in many seabird populations along Canada's coasts is occurring. Many of these losses will be due to HFOs, although even approximate proportions are not available. During nesting season, those birds that are oiled may expose their eggs to lethal doses of HFOs. Most seabirds on the east and west coasts are potentially exposed to oil during the non-nesting season when they spend most of their time at sea (Burger 1993b).

In addition to the variable oil toxicities, the potential impacts on hatching and mortality rates are also dependent on many variables, including the physical characteristics of the exposure scenario, the spill size and the biology and type of

seabird potentially affected (Albers 1980; Burger 1993a). The previous view was that detrimental population-level effects would only be significant for large to exceptionally large oil spills (> 1000 barrels) (RMRI 2007). However, an analysis of spill volume and seabird mortality by Burger (1993a) found little correlation between volume of oil spilled and mortality due to the many poorly understood variables affecting the gross number of birds killed by a spill. Small spills may be just as likely as large spills to significantly affect a seabird population, as the volume of the spill accounts for 24% of the variability in seabird mortality (Burger 1993a). It is estimated that up to 50% of some Canadian populations of species living off the south and east coasts of Newfoundland, such as the thick-billed murre, dovekie and northern gannet, could be affected if a spill of 1000 barrels of oil were to occur during sensitive time periods, such as nesting, in this habitat (RMRI 2007). As well, the area of ocean southwest of Vancouver Island is a particularly productive seabird habitat for many bird species, including common murres (*Uria aalge*) and Cassin's auklets (*Ptychoramphus aleuticus*) in winter, with upwards of 100 birds/km of transect and with Cassin's auklets, occasionally forming groups of thousands where feeding is particularly good (Burger 1993b; Burger 2003). Summer post-breeding numbers of many other birds are high due to the physical nature of the coastal shelf, promoting high densities of prey organisms. Seabird mortalities in this area have been found to be as high as 47 500 to 68 500 birds, as in the case of the Bunker C spill of 875 000 L from the barge *Nestucca* in 1988 (Burger 1993b).

9.1.3 Mammalian toxicity

Historical spills of HFOs have demonstrated that these substances can be detrimental to mammals (Warner 1969; Baker et al. 1981), although the cause of death of mammals is not often indicated and is likely due to the direct oiling of the mammal, in addition to ingestion. Harp seals that were covered with Fuel Oil No. 6 in the Gulf of St. Lawrence had difficulty swimming and are believed to have died from exhaustion (Warner 1969). At least 13 otters (*Lutra lutra)* died due to a Bunker C spill at the Sullom Voe oil terminal on Shetland Island (Baker et al. 1981). Other field reports indicate that, depending on the species present, other mammals such as muskrats and chipmunks can be affected (Smith 1976). In the case of the 1976 spill in the St. Lawrence, 79 mammals were affected (Smith 1976).

There is limited information on the effects of mammalian ingestion of HFOs. What exists is primarily based on mink, which is often used as a surrogate species. The ingestion of low concentrations of Bunker C during chronic exposures has been shown to have endocrine effects (Mohr et al. 2008, 2010; Schwartz et al. 2004a, 2004b) and reproductive effects (Mazet et al. 2001).

Mohr et al. (2008, 2010) found that HFO ingestion has sublethal effects at chronic exposure, which causes the development of enlarged adrenal glands in

male ranched mink (*Mustela vison*). There appeared to be no significant differences between the effects from exposure to artificially weathered and non-weathered HFOs. Because HFOs are already heavily refined, the most volatile components have been removed during the distillation process, similar to the removal of lightweight components by weathering (Mohr et al. 2010). Schwartz et al. (2004a, 2004b) found that effects of oil exposure at 500 ppm over 113–118 days led to sublethal effects, such as alterations to hepatic metabolism, adrenal physiology and perturbations in immune responses.

Fuel Oil No. 6 ingestion also affects the reproductive success of mammals. Mazet et al. (2001) used ranch-reared mink (*Mustela vison*) as a model to investigate the potential effects of Fuel Oil No. 6 on sea otters (*Enhydra lutris*). Mink were fed rations containing 500 ppm of Fuel Oil No. 6 (dose of 0.065 g/kg). Females that were exposed to Fuel Oil No. 6 produced only 0.7 kits/female, which was significantly lower than unexposed controls (5.3 kits/female). Once mature, kits born to females exposed to this substance had significantly reduced reproductive success (3.4 kits/female) in comparison to controls (5.3 kits/female). The authors suggest that sea otter populations consuming petroleum-contaminated food sources or colonizing previously oiled habitats will likely have reduced reproductive success.

9.1.4 Aquatic vegetation

Laboratory and field studies show that Fuel Oil No. 6 can have a range of effects on various plant species depending on the concentration and the species.

The *Arrow* spill into Chedabucto Bay in 1970 led to extensive mortalities of brown kelp (*Fucus spiralis*) on rocky shores and smooth cordgrass (*Spartina alterniflora*) in the lagoons (Thomas 1973, 1978).

Experimental oiling studies have shown that oiling affects aquatic vegetation through the creation of an impermeable film that blocks the stomata, thereby inhibiting gas exchange and photosynthesis (Meudec et al. 2005; Wernick et al. 2009). If the above-ground vegetation is coated with HFOs, fewer plants will survive (NOAA 2010). If the substrate is heavily oiled, the roots will likely die and plants will not regrow. Overall, however, laboratory and field studies show that plants can survive partial oiling (NOAA 2010).

Krebs and Tanner (1981) found that, when sediment hydrocarbon concentrations were below 2000 µg/g, *S. alterniflora* (a marine wetland grass) showed slight increases in stem height, density and above-ground biomass during the first growing season. However, at concentrations above 2000 µg/g, these effects decreased. For concentrations greater than 10 000 µg/g, most of the underground rhizomes were killed and there was little natural regrowth. The toxic effects may be immediate or delayed for one year, as was observed by Thomas

(1978) following the *Arrow* spill. Recovery, however, was evident two years later and populations appeared normal after five years (Thomas 1978; Vandermeulen 1977).

Fuel Oil No. 6 spilled in Lake Wabamun in 2005 occurred during the late growing season and winter senescent period, and was present in the abundant *Scirpus validus* beds in the eastern basin of the lake (Wernick et al. 2009). Productivity measures found that HFO exposure at this time did not cause large-scale changes to the *S. validus* communities (Wernick et al. 2009).

A CTV was not determined for aquatic vegetation, as there are more sensitive species found in the aquatic compartment.

9.1.5 Terrestrial compartment

Data on acute oral toxicity of Fuel Oil No. 6 to small mammals are presented in Table F-2 (Appendix F) and Appendix G (Summary of Health Effects Information). Results show that oral exposure of rats to Fuel Oil No. 6 is lethal only at high doses (5130 mg/kg-bw) (CONCAWE 1998) and is not considered to be likely in the wild (Table F-2 in Appendix F; Appendix G). Inhalation of Fuel Oil No. 4 vapours at 300 mg/m^3 was not lethal to rats (Cowan and Jenkins 1981). This pathway of exposure is not significant, due to the low vapour pressure of HFOs (CONCAWE 1998).

The *Canada-Wide Standards for Petroleum Hydrocarbons in Soil* was used as a data source for the quantification of effects of HFOs on terrestrial ecosystems. These standards were developed based on the consideration of four fractions of total petroleum hydrocarbons (TPH): F1 (C_6–C_{10}), F2 (> C_{10}–C_{16}), F3 (> C_{16}–C_{34}), F4 (> C_{34}), and assumes an 80:20 ratio of aliphatics to aromatics. Fraction 3 is most like HFOs. This system also uses four land-use classes (agricultural, residential, commercial, industrial) and two soil types (coarse-grained and fine-grained). The most sensitive land-use and soil type is typically agricultural coarse-grained soils. The lowest remedial standard for soil contact by non-human organisms (invertebrates, plants) for the F3 fraction is 300 mg/kg d.w. (dry weight) for coarse-grained agricultural or residential soil (CCME 2008). This value was used as the CTV for soil contact.

9.2 Ecological Exposure Assessment

9.2.1 Aquatic

To determine the PEC arising from ship transport, the volume of water predicted to be in contact with spilled oil was provided by a study conducted by the Risk

Management Research Institute (RMRI 2007). The area of a slick created within hazard zones around Newfoundland was estimated for specific volume ranges of oil using ocean spill dispersion models, and the volume of contacted water was then estimated by multiplying the area by 10 to represent the top 10 m of water. This represents a conservative estimate, as it assumes that all of the water is equally contacted by the petroleum product spilled.

For loading and unloading scenarios for ships, the volume of water in contact with oil from Hazard Zone 1 was used, as this region included loading and off-loading operations at Whiffen Head and the Come By Chance refinery. For the ship transport scenario, the estimated volume of water in contact with oil was the volume of water averaged over hazard zones 2 to 5 (the average volume of water for summer and winter for Hazard Zone 2 was used in this calculation).

In the case of loading and unloading of HFOs by ship in marine water, an estimated 13 120 L of HFOs, on average, are released in one event (Table 6-1). At an average density of 0.98 kg/L (Environment Canada c2001), this is equivalent to 83 barrels of HFOs and is therefore expected to be in contact with 1.5×10^{11} L of water (Table F-3 in Appendix F). This volume is estimated from the enclosed waters found at wharves and loading terminals. The resulting concentration in water would be 0.09 mg/L (1.3×10^{10} mg / 1.5×10^{11} L), which is considered the marine PEC for ship loading and unloading.

In the case of the transportation of HFOs by ship in marine water, an estimated 13 120 L of HFOs, on average, are released in one event (Table 6-1). At an average density of 0.98 kg/L (Environment Canada c2001), this is equivalent to 83 barrels of HFOs and is therefore expected to be in contact with 6.3×10^{12} L of water (Table F-3 in Appendix F). This volume is estimated from the open ocean of Placentia Bay. The resulting concentration in water would be 0.002 mg/L (1.3×10^{10} mg / 6.3×10^{12} L), which is considered the marine PEC for ship transport.

In the case of the loading and unloading of HFOs by ship in freshwater, an estimated 15 090 L of HFOs, on average, are released in one event (Table 6-1). At an average density of 0.98 kg/L (Environment Canada c2001), this is equivalent to 95 barrels of HFOs and is therefore expected to be in contact with 1.5×10^{11} L of water (Table F-3 in Appendix F). This volume is estimated from the enclosed waters found at wharves and loading terminals. The resulting concentration in water would be 0.1 mg/L (1.5×10^{10} mg / 1.5×10^{11} L), which is considered the freshwater PEC for ship loading and unloading.

In the case of the transportation of HFOs by ship, an estimated 15 090 L of HFOs, on average, are released in one event to freshwater (Table 6-1). At an average density of 0.98 kg/L (Environment Canada c2001), this is equivalent to 95 barrels of HFOs and is therefore expected to be in contact with 6.3×10^{12} L of water (Table F-3 in Appendix F). This volume is estimated from the open ocean

of Placentia Bay. The resulting concentration in water would be 0.002 mg/L (1.5×10^{10} mg / 6.3×10^{12} L), which is considered the freshwater PEC for ship transport.

9.2.2 Terrestrial

It is estimated that there will be ≤ 1 release event per year in total for train loading, unloading and transport, and ≤ 1 release event per year in total for truck loading, unloading and transport based on historical release information from the NEMISIS database (Environment Canada 2011a). The majority of spill events are expected to occur at industrial facilities. These infrequent releases likely occur on a hard surface and not on soil, and are considered to be of low ecological concern. In terms of pipeline transport of these HFOs, it is expected that there would be approximately one release event per year based on historical release information from the NEMISIS database (Environment Canada 2011a).

Releases to air were not considered in the ecological portion of this assessment, as the volatility of Fuel Oil No. 6 is extremely low. A headspace analysis and microextraction procedure using a ratio of 50 mL oil per L of water (1:20) determined that Bunker C contributed very little, if any, volatile material to the water soluble fraction (0 mg/L for headspace extraction and 1.7 mg/L for microextraction) (Murray et al. 1984). Thus, the concentrations of volatile components that are expected to be lost to the atmosphere are extremely small.

9.3 Characterization of Ecological Risk

The approach taken in this ecological screening assessment was to examine available scientific information and develop conclusions based on a weight-of-evidence approach as required under CEPA 1999. For each endpoint organism, an estimate of the potential to cause adverse effects and predicted no-effect concentration (PNEC) was determined. The PNEC is the lowest CTV for the organism of interest divided by an appropriate assessment factor. Also, a PEC was determined for each aquatic exposure scenario. A risk quotient (defined as RQ = PEC/PNEC) was calculated for each endpoint organism and is an important line of evidence in evaluating the potential risk to the environment.

For the marine exposure scenario during loading, transport and unloading, the CTV was chosen to be the 48-hour acute LC_{50} of 0.9 mg/L for *Mysidopsis almyra* (mysid shrimp) (Table F-1a in Appendix F). An assessment factor of 10 was used for all marine scenarios to account for the extrapolation of laboratory-to-field effects. For the freshwater exposure scenarios, the selected CTV was the 96-hour acute EC_{50} (immobilization) of 4.1 mg/L for *Daphnia magna* for ship loading/unloading and transport (Table F-1a in Appendix F). An assessment

factor of 10 was also used to account for extrapolation of laboratory-to-field effects.

Table 9-1 provides a summary of the risk quotients for the HFOs for aquatic exposure scenarios. Only spills to marine water during the loading/unloading of ships were determined to be potentially harmful to fish, as the RQ is equal or greater than 1.

Table 9-1. Risk quotients calculated for HFOs based on average spill volumes for aquatic exposure scenarios

Compartment affected	Organism	PEC (mg/L)	CTV (mg/L)	Assess-ment factor	PNEC (mg/L)	Risk quotient
Marine (loading/ unloading)	*Mysidopsis almyra*	0.09	0.9	10	0.09	1
Marine (transport)	*Mysidopsis almyra*	0.002	0.9	10	0.09	0.02
Freshwater (loading/ unloading)	*Daphnia magna*	0.1	4.1	10	0.4	0.25
Freshwater (transport)	*Daphnia magna*	0.002	4.1	10	0.4	0.005

For all aquatic spill scenarios, the spill volume required to obtain a risk quotient equal to 1 was determined (Table 9-2). The frequency of spills above that threshold was determined from the Environment Canada NEMISIS database (Environment Canada 2011a).

Table 9-2. Spill volumes required to create harmful conditions to aquatic organisms and the proportion of reported spills above this threshold volume

Compartment affected	Spill volume required to obtain RQ = 1 (threshold volume) (L)	Proportion of reported spills above the threshold volume (%)	Approximate number of spills per year above the threshold volume
Marine (loading/unloading)	13 900	13	1
Marine (transport)	890 000	0	0
Freshwater (loading/unloading)	61 500	11	< 1

Freshwater (transport)	7 090 000	0	0

There were 108 spills to marine waters and 53 spills to freshwater in Canada from 2000 to 2009 (Environment Canada 2011a).

For ship transport in marine and freshwater, spill volumes of 890 000 L (890 tonnes) and approximately 7 million litres (7000 tonnes) of HFOs, respectively, are required to obtain a risk quotient of 1 for aquatic organisms. None of the reported spills from 2000 to 2009 was greater than these threshold volumes during ship transport; therefore, the expected number of spills per year above this volume is 0. Thus, spills to freshwater and marine waters during ship transport are not expected to pose harm to aquatic organisms.

There is a greater percentage of reported spills above the threshold volume during the loading/unloading of ships in marine and freshwater environments (13% for marine; 11% for freshwater) (Table 9-1). Due to the low frequency of events, this yields 1 expected spill above the threshold volume per year in marine waters, and less than 1 spill per year in freshwater. The narrow scope of the reporting requirements to NEMISIS may lead to a low estimation of the frequency of spills, though this is not as great a concern for spills to water as NEMISIS does require the reporting of marine spills or those that contravene the *Fisheries Act*. However, the NEMISIS database may also capture other fuel oils aside from Fuel Oil No. 4, Fuel Oil No. 6 and Residual Fuel Oil, as all spills were generically labelled as bunker, which might overestimate spills. Thus, based on the relatively low number of spills per year above the threshold volumes required for an RQ more than 1, spills of these fuel oils to water during loading and unloading are considered to be infrequent and pose a low risk of harm to aquatic organisms.

These spill volumes were calculated based on models developed by RMRI (2007) relating the volume spilled and concentration of petroleum substance in the water. These models take into consideration the dispersion of the petroleum substance spilled, and therefore, the calculated spill volume relating to a risk quotient of 1 is not for the acute, initial exposure to the spilled material. It is recognized that local, acute effects may occur during the initial phase of a spill before significant dispersion occurs.

Aquatic birds have not been included in the RQ analysis due to the lack of toxicity information for these HFOs to birds. However, field reports and experiments have shown that these HFOs are hazardous to aquatic birds through ingestion (CONCAWE 1998; Ainley 1978, 1981; Michigan 2010), contact with feathers (Environment Canada 2011b) and contact with eggs (CONCAWE 1998; Szaro 1979; Grau et al. 1977; Wootton et al. 1979). Due to the very low frequency of spills during transport, harm to birds is not expected.

From 2000 to 2009, the NEMISIS database had relatively few spill reports of Bunker C from trucks (32 spills) and trains (11 spills). Considering the cause of and reasons for each spill by train and truck, less than 1 spill per year is expected for each during loading, transport and unloading. No attempt was made to determine the residual oil left following remediation efforts, due to lack of data. Thus, potential terrestrial impacts from truck and train transport of these 3 CAS RNs are likely to be of low ecological concern due to their low frequency of spill. Likewise, the estimated spills from truck loading and unloading would likely occur on a hard surface and not on soil. Thus, exposure to soil is unlikely.

No exposure scenarios were developed for soil or air due to the limited releases into these environmental compartments.

These CAS RNs are also transported by pipeline. With 13 spills of Bunker C during pipeline transport reported from 2000 to 2009 to the NEMISIS database (Environment Canada 2011a), it is expected that there would only be approximately one release event per year. Because of the low frequency of pipeline releases of Bunker C, spills of these HFOs from pipelines are considered to pose a low risk of harm to terrestrial organisms.

Overall, there is a low risk of harm to aquatic (fish, invertebrates, algae) and soil (invertebrates, plants) organisms given the current frequency and size of Fuel Oil No. 4, Fuel Oil No. 6 and Residual Fuel Oil releases to aquatic, marine and terrestrial environments.

Based on the available information, these HFOs contain components, such as some PAHs, that may persist in air and undergo long-range transport to remote regions. They also contain some components that might persist in soil, water and/or sediment, thus increasing the duration of exposure to organisms. The HFOs assessed in this report are also expected to contain components that are highly bioaccumulative. Studies suggest that most components will not likely biomagnify in food webs; however, there is some indication that alkylated PAHs might.

In general, fish can efficiently metabolize aromatic compounds. There is some evidence that alkylation increases the bioaccumulation of naphthalene (Neff et al. 1976; Lampi et al. 2010), but it is not known if this can be generalized to larger PAHs or if any potential increase in bioaccumulation due to alkylation will be sufficient to exceed a BAF/BCF of 5000.

Some lower trophic level organisms (i.e., invertebrates) appear to lack the capacity to efficiently metabolize aromatic compounds, resulting in high bioaccumulation potential for some aromatic components as compared to fish. This is the case for some three-, four-, five-, and six-ring PAHs, which were bioconcentrated to high levels (BCF greater than 5000) by invertebrates (e.g., *Daphnia*, molluscs) but not by fish. There is potential for such bioaccumulative

components to reach toxic levels in organisms if exposure is continuous and of sufficient magnitude, though this is unlikely in the water column following a spill scenario due to relatively rapid dispersal. However, some of these components can also persist in sediments for long periods of time, which can increase the exposure duration of benthic invertebrates to these components.

Bioaccumulation of aromatic compounds might be lower in natural environments than what is observed in the laboratory. PAHs may sorb to organic material suspended in the water column (dissolved humic material), which decreases their overall bioavailability primarily due to an increase in size. This has been observed with fish (Weinstein and Oris 1999) and *Daphnia* (McCarthy et al. 1985).

Based on the available information, these HFOs are moderately to highly toxic to aquatic organisms (fish, invertebrates, algae), as well as to seabirds and their eggs.

A key consideration in characterizing the ecological risks of these substances is the nature, extent and frequency of spills. Spills during handling of Fuel Oil No. 4, Fuel Oil No. 6 or Residual Fuel Oil have the potential to cause harm to aquatic life in the confined marine waters around loading/unloading wharves. However, based on the low frequency of (less than one per year) and resulting low exposure to the environment from spills, there is low risk of harm to the environment.

Considering all available lines of evidence presented in this screening assessment, there is a low risk of harm to organisms and the broader integrity of the environment from these substances. It is concluded that Fuel Oil No. 4, Fuel Oil No. 6 and Residual Fuel Oil (CAS RNs 68476-31-3, 68553-00-4 and 68476-33-5) do not meet the criteria under paragraphs 64(*a*) or (*b*) of CEPA 1999, as they are not entering the environment in quantities or concentrations or under conditions that have or may have immediate or long-term harmful effects on the environment or its biological diversity, or that constitute or may constitute a danger to the environment on which life depends.

9.4 Uncertainties in Evaluation of Ecological Risk

This analysis addresses the uncertainty associated with each component of the current assessment, including but not limited to selection of representative structures and quantification, exposure estimation, effects estimation and risk characterization.

All modelling of the substances' physical-chemical properties and persistence, bioaccumulation and toxicity characteristics is based on chemical structures. As Fuel Oil No. 4, Fuel Oil No. 6 and Residual Fuel Oil are considered to be UVCBs,

they cannot be represented by a single, discrete chemical structure. The specific chemical composition of these three CAS RNs is not well defined. HFO streams under the same CAS RNs can vary significantly in the number, identity and proportion of constituent compounds, depending on operating conditions, feedstocks and processing units. Therefore, for the purposes of modelling, a suite of representative structures that provide average estimates for the entire range of components likely present was identified. Specifically, these structures were used to assess the fate and hazard properties of these HFOs. Given that more than one representative structure may be used for the same carbon range and type of component, it is recognized that structure-related uncertainties exist for this substance. In order to represent the range in physical-chemical characteristics, the physical-chemical properties of 45 representative structures were used to estimate the overall behaviour of these HFOs. Given the large number of potential permutations of the type and percentages of the structures in HFOs, there is uncertainty in the results associated with modelling.

There is also uncertainty in the use of historical spills information from the Emergency NEMISIS database (Environment Canada 2011a). Reporting requirements to NEMISIS are limited to releases involving or affecting a federal agency or department, a federal government facility or undertaking, or Aboriginal land; or releases that contravene CEPA 1999 or the *Fisheries Act*; releases that affect fish, migratory birds or species at risk or that impact an interprovincial or international boundary; and releases from marine vessels. Therefore, NEMISIS likely underreports spills nationally, especially spills to land.

Due to the lack of information available for Fuel Oil No. 4 and Residual Fuel Oil, most data used throughout this screening assessment are based on Fuel Oil No. 6. Fuel Oil No. 4 and Residual Fuel Oil are a blend of distillate and heavy (residual) fuel oils and are presumed to be similar in properties to Fuel Oil No. 6.

This assessment involves the prediction of effects on biota using measured model inputs and modelled accumulation or exposures. The process typically relies on modelled exposures for organisms at higher trophic levels. However, all models are simplifications of natural systems or processes, and therefore rely on a number of assumptions. These, in turn, create uncertainties in the outcomes.

The BAF model calculations were derived from a large database of measured BAF values from the Great Lakes for chemicals that are poorly metabolized (e.g., polychlorinated biphenyls [PCBs]). With metabolic biotransformation, the BAF model predictions are in general agreement with measured BAFs in fish. The model may not adequately capture biotransformation at the first trophic level for chemicals that are readily biotransformed in invertebrates and plankton. Many petroleum hydrocarbons are readily metabolized, somewhat by invertebrates and at much higher levels in fish.

This report used present knowledge and judgement to determine the PNECs for Fuel Oil No. 4, Fuel Oil No. 6 and Residual Fuel Oil, for which generic assessment factors were applied. Assessment factors are not intended as mathematical absolutes, but rather as tools to address data that are surrounded by some unquantifiable level of uncertainty.

10. Potential to Cause Harm to Human Health

10.1 Exposure Assessment

The characterization of risk to human health of potential exposure to Fuel Oil No. 4, Fuel Oil No. 6 and Residual Fuel Oil considers their end uses in Canada.

These HFO substances are distinguished by their pour points and viscosity requirements as outlined in the CAS RN descriptions (NCI 2006). These properties determine the applications and types of combustion devices for the fuels: they can be used in burners, boilers, generators and/or engines. Refineries produce and consume these fuels on site, and they can also be used in electricity and steam generation by utilities and industry, and in other energy applications (Table C-2 in Appendix C). The bulk of the HFOs manufactured in or imported into Canada are combusted in the manufacturing sector (specifically pulp and paper), for marine transportation and for commercial/institutional heating (Table C-3 in Appendix C) (Statistics Canada 2007). The consumption pattern is predominantly industrial uses of HFOs and very limited residential use.

Fuel Oil No. 4, Fuel Oil No. 6 and Residual Fuel Oil are not marketed to the general population; these fuels require large specialized combustion equipment for heating, thus precluding small-scale residential applications and limiting use by the general population (Statistics Canada 2007). Residential use accounts for only 0.4% of the consumption pattern of HFOs (Table C-3 in Appendix C), and is restricted to multi-unit building heating systems due to the nature of the burner/boiler equipment required. Access of residents to these heating systems, and thus to the fuels, is therefore unlikely (New Brunswick 2009). Accordingly, neither dermal nor oral exposures are expected for the general population of Canada (CONCAWE 1998; Statistics Canada 2007).

It has been noted that Fuel Oil No.4, Fuel Oil No. 6 and Residual Fuel Oil may sometimes be used in low quantities as cleaning solvents for removing oil-based material from tools or hands. However, CONCAWE (1998) has indicated that this use is unlikely, given the viscosity, colour and odour of these fuels. Therefore, the use of HFOs as cleaning solvents is not considered further.

Accidental ingestion of HFOs is highly unlikely, given the physical properties of these substances, including colour, malodour and viscosity (CONCAWE 1998; Statistics Canada 2007).

Fuel Oil No. 4, Fuel Oil No. 6 and Residual Fuel Oil have very low vapour pressures and are used most often at ambient temperatures (CONCAWE 1998); thus significant vapour releases to air, resulting in inhalation exposures for the general population, are not expected. However, vapours may be released upon heating Fuel Oil No. 6 prior to transport or use. The use profile for this substance indicates that it is concentrated in industry, marine transportation and the utilities sector; therefore, there is little potential for exposure within the general population of Canada (Statistics Canada 2007; CONCAWE 1998).

Potential exposures to HFO substances from industrial uses, storage and/or transport between facilities were previously considered in the Stream 1 and Stream 2 HFO Screening Assessment Reports (Environment Canada, Health Canada 2011, 2013), and the conclusions of these assessments are considered to apply to the Stream 3 HFO CAS RNs. Exposure of the general population to these substances from on-site consumption, storage and/or transportation is considered to be negligible.

Confidence in the exposure assessment, based on uses and properties of HFOs, is high despite a lack of monitoring data. The specialized equipment required for combustion of HFOs severely restricts residential and personal use. Additionally, confirmation from industry on the formulation and availability of Fuel Oil No. 4 in Canada validates the expectation of limited use and potential exposure of the general population only where special-order products are accessed (personal communication, phone conversation May 28, 2010, between Shell Canada and Oil, Gas and Alternative Energy Division, Enivornment Canada, unreferenced).

10.2 Health Effects Assessment

A limited number of studies were available to evaluate the health effects of Fuel Oil No. 4, Fuel Oil No. 6 and Residual Fuel Oil; thus, an adequate toxicological dataset unique to these substances could not be obtained. Health effects data were therefore pooled across related HFO substances to generate a comprehensive profile for the three HFOs considered herein. Appendix G contains an overview of the available health effects information in laboratory animals. Key studies are summarized below.

HFOs have low acute toxicity in laboratory animals. Male and female rats were exposed to 2100, 3300 and 4800 mg/m^3 Residual Fuel Oil aerosols. Effects included laboured breathing, gasping and reduced activity at all levels, and the median lethal concentration (LC_{50}) was determined to be 4100 mg/m^3 (Bio/dynamics Inc. 1987). Fuel Oil No. 6 exhibited oral median lethal doses

(LD_{50}) in rats of 5130 to > 25 000 mg/kg-body weight (bw). Other oral LD_{50} values for related HFO substances ranged from > 2000 to 5898 mg/kg-bw in rats. A dermal LD_{50} value for Fuel Oil No. 4 in mice was > 40 000 mg/kg-bw. Fuel Oil No. 6 exhibited dermal LD_{50} values ranging from > 4940 to > 5350 mg/kg-bw in rabbits. Minimal to moderate skin irritation was observed in all cases of acute dermal exposure (API 2004; CONCAWE 1996, 1998; U.S. EPA 2005; European Commission 2000b).

One study was identified that assessed the health effects of Fuel Oil No. 4 after repeated inhalation exposures. A lowest-observed-adverse-effect concentration (LOAEC) of 50 to 300 mg/m^3 was established based on decreased body weight gain in a subchronic study that exposed male and female rats to 50 or 300 mg/m^3 for 90 days (the concentration at which this effect was observed was not specified) (Cowan and Jenkins 1981). In a related study, decreased body weights and increased liver weights were observed after exposure of male and female Fischer 344 rats to CAS RN 64742-90-1 at 540 or 2000 mg/m^3 for 9 days (Gordon 1983).

Multiple dermal studies of varying lengths have been conducted for Fuel Oil No. 4, Fuel Oil No. 6 and Residual Fuel Oil. These studies ranged from 12 days to 60 weeks, with doses of 250 to 40 000 mg/kg-bw per day in mice, rats and rabbits. Selected effects included increased mortality; decreased body weight gain, body weight and food consumption; changes in spleen, liver and kidney weights; macroscopic renal lesions; extramedullary splenic haematopoiesis; anemia; karyomegaly, multifocal necrosis and centrilobular vacuolar degeneration in the liver; and epithelial hyperplasia of the urinary bladder mucosa. Significant skin irritation and injury were also observed at the application sites in all studies (Schultz et al. 1981; Easley et al. 1982; NTP 1986; API 1980a, 1980b, 1980c, 1980d; UBTL 1987, 1988).

Health effects were noted in pregnant CD rats exposed dermally to CAS RN 64741-62-4 during gestation. A lowest-observed-adverse-effect level (LOAEL) of 1 mg/kg-bw per day was identified based on decreases in body weight gain, body weight, food consumption and gravid uterine weight, as well as the occurrence of red vaginal exudates (Hoberman et al. 1995). In other studies, a LOAEL of 8 mg/kg-bw per day was established based on increased liver weights, reduced platelet counts and moderate skin irritation after subchronic exposure of male and female Sprague-Dawley rats to CAS RNs 64741-62-4 or 64741-81-7 (Feuston et al. 1994, 1997; Mobil 1988, 1994b). Other effects observed in these studies included increased mortality; decreased body weight gain, body weight and thymus weight; decreased thymic lymphoid cells; and aberrant serum chemistry and haematology.

It is noted that systemic effects were observed for related HFO substances at low dermal exposures (1 and 8 mg/kg-bw); however, no studies were found that examined Fuel Oil No. 4, Fuel Oil No. 6 or Residual Fuel Oil at doses lower than

250 mg/kg-bw per day. It is pertinent to note, however, that several of these Fuel Oil No. 4, Fuel Oil No. 6 and Residual Fuel Oil studies did not observe systemic effects at 250 mg/kg-bw per day, suggesting that some of the related HFO substances may have higher dermal toxicities than the three HFO CAS RNs considered herein.

One oral study conducted in pregnant Sprague-Dawley rats identified a LOAEL of greater than or equal to 125 mg/kg-bw based on decreased maternal body weight gain and thymus weight after administration of CAS RN 64741-62-4 during gestation (Feuston and Mackerer 1996).

In vivo genotoxicity studies were identified for related HFO substances. Positive results were observed for CAS RNs 64742-90-1 and 64741-62-4 for micronuclei induction and unscheduled deoxyribonucleic acid (DNA) synthesis (UDS) when administered to mice and rats via oral gavage, respectively (Khan and Goode 1984; API 1985a). Positive results were also observed for CAS RN 64741-62-4 for sister chromatid exchange when administered to mice via intraperitoneal (i.p.) injection (API 1985b). Negative results were observed for CAS RNs 64741-57-7 and 64741-62-4 for micronuclei induction and chromosomal aberrations in rats when applied dermally or administered via i.p. injection (Mobil 1987d; API 1985c).

In vitro genotoxicity for Fuel Oil No. 4 and Fuel Oil No. 6 were negative for the Ames, sister chromatid exchange and mouse lymphoma assays, as well as for forward mutations and for inhibition of morphological transformation (NTP 1986; Schultz et al. 1981; Vandermeulen et al. 1985; Farrow et al. 1983; Vandermeulen and Lee 1986; Blakeslee et al. 1983). Positive results were observed for related HFO substances, including in the Ames, modified Ames and mouse lymphoma assays, as well as for cell transformation and UDS (Brecher and Goode 1983, 1984; Blackburn et al. 1984, 1986; API 1985c, 1985d, 1986a; Mobil 1985; Feuston et al. 1994).

Fuel Oil No. 4 was classified by the European Commission as a Category 3 carcinogen (R40: *limited evidence of a carcinogenic effect*), and Fuel Oil No. 6 and Residual Fuel Oil were classified as Category 2 carcinogens (R45: *may cause cancer*) (European Commission 1994; ESIS c1995–2012). The European Commission also adopted the United Nations' Globally Harmonized System of Classification and Labelling of Chemicals, which classified Fuel Oil No. 4 as a Category 2 carcinogen (H351: *suspected of causing cancer*) and Fuel Oil No. 6 and Residual Fuel Oil as Category 1B carcinogens (H350: *may cause cancer*) (European Commission 2008). The International Agency for Research on Cancer (IARC) has determined the overall classification for residual (heavy) fuel oils to be Group 2B (*possibly carcinogenic to humans*) (IARC 1989a).

The carcinogenic potential of Fuel Oil No. 4 was investigated in one skin painting study in mice. An increase in the number of mice with skin tumours (squamous

cell papillomas and carcinomas) occurred after two years dermal exposure to 250 or 500 mg/kg-bw of Fuel Oil No. 4 (NTP 1986). Thermally cracked Residual Fuel Oil and a blend of straight-run and Residual Fuel Oil were concluded to be dermal carcinogens after lifetime exposure of mice to approximately 592 mg/kg-bw (Exxon Biomedical Sciences Inc. 1992). In a skin painting study of a related HFO (CAS RN 64741-62-4), male mice were exposed to doses of 8.4, 16.8, 42, 83.8 or 167.6 mg/kg-bw, 3 times per week for life. Significant skin tumour formation was observed at all doses and increased in a dose-dependent manner (McKee et al. 1990).

In a tumour initiation study, male mice were dermally exposed to CAS RN 64741-62-4 at a dose of 16.8 mg/kg-bw for 5 consecutive days (followed by exposure to a promotion agent for 25 weeks). Significant skin tumour formation was observed at this dose with a latency period of 16 weeks. In the corresponding promotion study, a significant increase in the number of mice with gross masses (and shortened latency periods) was observed, suggesting possible weak promoting activity; however, there was no increase in histologically confirmed tumour incidence (API 1989).

The results indicate that, in general, HFOs exhibit carcinogenic activity in mice via the dermal route of exposure.

It is recognized that HFOs may contain appreciable concentrations of components that exhibit carcinogenic activity as single substances, such as certain types of PAHs. The Government of Canada previously completed a human health risk assessment of five PAHs, including a critical review of relevant data, under the Priority Substances Program. Based primarily on the results of carcinogenicity bioassays in animal models, these PAHs (benzo[*a*]pyrene, benzo[*b*]fuoranthene, benzo[*j*]fluoranthene, benzo[*k*]fluoranthene and indeno[*1,2,3-cd*]pyrene) were classified as Probably Carcinogenic to Humans (i.e., substances for which there is considered to be some probability of harm for the critical effect at any level of exposure), and considered to be "toxic" as defined under paragraph 11(*c*) of the *Canadian Environmental Protection Act* (Canada 1994). Due to the lack of exposure to HFOs, evaluating the contribution of HFO components to carcinogenic activity is outside the scope of the current assessment.

A reproductive dermal LOAEL of 1.0 mg/kg-bw per day was identified in pregnant CD rats exposed to CAS RN 64741-62-4 during gestation (Hoberman et al. 1995). Effects included decreased live fetuses and increased incidences of resorptions, early resorptions and percent of dead or resorbed conceptuses per litter. Fetal developmental variations were also observed in this study, but were determined not to be substance-related. A developmental dermal LOAEL of 8 mg/kg-bw per day was identified in pregnant Sprague-Dawley rats exposed to CAS RN 64741-62-4 during gestation (Feuston et al. 1989; Mobil 1987e). Effects

included fetal external abnormalities, including cleft palate, micrognathia (shortened lower jaw) and kinked tail.

It is noted that, as a group, HFOs demonstrated significant health effects. However, there was a discrepancy between the three HFOs considered herein and the related HFO substances regarding their genotoxic potential (Fuel Oil No. 4 and Fuel Oil No. 6 were negative, whereas related HFO substances were positive) and potency (dermal effects were established at 250 mg/kg-bw for the three HFOs but at 1 and 8 mg/kg-bw for related HFOs). Thus, it is possible that the health effects information presented in Appendix G is conservative in terms of representing Fuel Oil No. 4, Fuel Oil No. 6 or Residual Fuel Oil.

10.3 Characterization of Risk to Human Health

Fuel Oil No. 4 and Fuel Oil No. 6 were identified as high priorities for action during categorization of the DSL because they were considered to present a high hazard to human health and were determined to present greatest potential or intermediate potential for exposure of individuals in Canada. Residual Fuel Oil was identified as a high hazard to human health. A critical effect for the initial categorization of these substances was carcinogenicity, based on classifications by international agencies and on a limited number of skin painting studies in laboratory animals that reported skin tumour development following chronic dermal application of Fuel Oil No. 4 or Residual Fuel Oil (NTP 1986; Exxon Biomedical Sciences Inc. 1992). These substances are classified as Category 2 or 3 carcinogens by the European Commission (European Commission 1994; ESIS c1995–2012), Category 1B or 2 carcinogens using the Globally Harmonized System of Classification and Labelling of Chemicals, as adopted by the European Commission (European Commission 2008), and Group 2B carcinogens by IARC (IARC 1989a).

Fuel Oil No. 4, Fuel Oil No. 6 and Residual Fuel Oil are essentially limited to use by industries for heat and energy production and for marine transportation. However, they can also be used to heat some multi-unit residential buildings. In such cases, access to the fuels by residents is not expected. HFOs are not marketed to the public and, because they have very low vapour pressures, exposure of the general population is not expected. Therefore, the risk to human health from these substances is considered to be low.

10.4 Uncertainties in Evaluation of Risk to Human Health

As Fuel Oil No. 4, Fuel Oil No. 6 and Residual Fuel Oil are UVCBs, their specific compositions are only broadly defined. Substances and different batches of the same CAS RN can vary depending on feedstocks, processing units and refining conditions, and blending streams used to meet the final product specifications.

This variability affects the identities, levels and proportions of constituent compounds in the samples, making it difficult to obtain a truly representative toxicological dataset, as the physical-chemical properties are not narrowly defined.

11. Conclusion

Considering all available lines of evidence presented in this screening assessment, there is a low risk of harm to organisms and the broader integrity of the environment from these substances. It is concluded that Fuel Oil No. 4, Fuel Oil No. 6 and Residual Fuel Oil (CAS RNs 68476-31-3, 68553-00-4 and 68476-33-5) do not meet the criteria under paragraphs 64(*a*) or (*b*) of CEPA 1999, as they are not entering the environment in a quantity or concentration or under conditions that have or may have immediate or long-term harmful effects on the environment or its biological diversity, or that constitute or may constitute a danger to the environment on which life depends.

Exposure of the general population to Fuel Oil No. 4, Fuel Oil No. 6 and Residual Fuel Oil is not expected based on the limited residential use and restricted access to the fuels. Thus, the risk to human health is considered to be low. Accordingly, it is concluded that Fuel Oil No. 4, Fuel Oil No. 6 and Residual Fuel Oil (CAS RNs 68476-31-3, 68553-00-4 and 68476-33-5) do not meet the criteria under paragraph 64(*c*) of CEPA 1999, as they are not entering the environment in a quantity or concentration or under conditions that constitute or may constitute a danger in Canada to human life or health.

It is therefore concluded that Fuel Oil No. 4, Fuel Oil No. 6 and Residual Fuel Oil (CAS RNs 68476-31-3, 68553-00-4 and 68476-33-5) do not meet the criteria set out in section 64 of CEPA 1999.

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Appendix A: Petroleum Substance Grouping

Table A-1. Description of the nine groups of petroleum substances

Group[a]	Description	Example
Crude oils	Complex combinations of aliphatic and aromatic hydrocarbons and small amounts of inorganic compounds, naturally occurring under the Earth's surface or under the sea floor	Crude oil
Petroleum and refinery gases	Complex combinations of light hydrocarbons primarily from C_1 to C_5	Propane
Low boiling point naphthas	Complex combinations of hydrocarbons primarily from C_4 to C_{12}	Gasoline
Gas oils	Complex combinations of hydrocarbons primarily from C_9 to C_{25}	Diesel fuel
Heavy fuel oils	Complex combinations of heavy hydrocarbons primarily from C_{20} to C_{50}	Fuel Oil No. 6
Base oils	Complex combinations of hydrocarbons primarily from C_{15} to C_{50}	Lubricating oils
Aromatic extracts	Complex combinations of primarily aromatic hydrocarbons from C_{15} to C_{50}	Feedstock for benzene production
Waxes, slack waxes and petrolatum	Complex combinations of primarily aliphatic hydrocarbons from C_{12} to C_{85}	Petrolatum
Bitumen or vacuum residues	Complex combinations of heavy hydrocarbons having carbon numbers greater than C_{25}	Asphalt

[a] These groups were based on classifications developed by CONCAWE and a contractor's report presented to the Canadian Petroleum Products Institute (CPPI) (Simpson 2005).

Appendix B: Physical-chemical Data Tables for Fuel Oil No. 4, Fuel Oil No. 6 and Residual Fuel Oil

Table B-1. Physical-chemical properties for representative structures of Fuel Oil No. 4, Residual Fuel Oil and Fuel Oil No. 6[a]

Alkanes

Chemical class, name (CAS RN)	HFO represented	Boiling point (°C)	Melting point (°C)	Vapour pressure (Pa)[b]
C_{12} dodecane (112-40-3)	68476-31-3	216.3 (expt.)	-9.6 (expt.)	18.0 (expt.)
C_{15} pentadecane (629-62-9)	68476-31-3 68553-00-4 68476-33-5	271 (expt.)	9.9 (expt.)	0.5 (expt.)
C_{20} eicosane (112-95-8)	68476-31-3 68553-00-4 68476-33-5	343 (expt.)	37 (expt.)	6.2×10^{-4} (expt.)
C_{30} triacontane	68476-31-3 68553-00-4 68476-33-5	450 (expt.)	65.8 (expt.)	3.6×10^{-9} (expt.)
C_{50}	68476-31-3 68553-00-4 68476-33-5	548 (expt.)	87 (expt.)	2×10^{-7}

Isoalkanes

Chemical name (CAS RN)	HFO represented	Boiling point (°C)	Melting point (°C)	Vapour pressure (Pa)[b]
C_{12} 2,3-dimethyl decane (17312-44-6)	-	181.4	-43.0	165.0
C_{15} 2-methyl tetradecane (1560-95-8)	68476-31-3 68553-00-4 68476-33-5	250	1.5	5.8
C_{20} 3-methyl nonadecane (6418-45-7)	68476-31-3 68553-00-4 68476-33-5	326	40.0	0.1

Chemical name (CAS RN)	HFO represented	Boiling point (°C)	Melting point (°C)	Vapour pressure (Pa)[b]
C_{30} hexamethyl tetracosane (111-01-3)	68476-31-3 68553-00-4 68476-33-5	408	75.0	0.04
C_{50}	-	675.5	294.6	5.1×10^{-10}

One-ring cycloalkanes

Chemical name (CAS RN)	HFO represented	Boiling point (°C)	Melting point (°C)	Vapour pressure (Pa)[b]
C_{12} *n*-hexylcyclo hexane (4292-75-5)	-	224 (expt.)	-43 (expt.)	15.2 (expt.)
C_{15} nonylcyclo hexane (2883-02-5)	68476-31-3 68553-00-4 68476-33-5	282 (expt.)	-10 (expt.)	0.3 (expt.)
C_{20} tetradecylcyclo hexane (1795-18-2)	68476-31-3 68553-00-4 68476-33-5	360 (expt.)	24 (expt.)	0.02
C_{30} 1,5-dimethyl-1-(3,7,11,15-tetramethyl octadecyl) cyclohexane	68476-31-3 68553-00-4 68476-33-5	421	103	1.5×10^{-4}
C_{50}	68553-00-4	674	294	5.6×10^{-13}

Two-ring cycloalkanes

Chemical name (CAS RN)	HFO represented	Boiling point (°C)	Melting point (°C)	Vapour pressure (Pa)[b]
C_{12} dicyclohexyl (92-51-3)	68476-31-3 68553-00-4 68476-33-5	238 (expt.)	4 (expt.)	14.4 (expt.)
C15 pentamethylde	68476-31-3 68553-00-4	187.3 (expt.)	-30.3 (expt.)	163 (expt.)

Chemical name (CAS RN)	HFO represented	Boiling point (°C)	Melting point (°C)	Vapour pressure (Pa)[b]
calin (91-17-8)	68476-33-5			
C_{20} 2,4-dimethyl octyl-2-decalin	68476-31-3 68553-00-4 68476-33-5	324	41	0.1
C_{30} 2,4,6,10,14 pentamethyl dodecyl-2-decalin	68476-31-3 68553-00-4 68476-33-5	420	106	0.0001
C_{50}	68553-00-4	664	289	1.2×10^{-18}

Polycycloalkanes

Chemical name (CAS RN)	HFO represented	Boiling point (°C)	Melting point (°C)	Vapour pressure (Pa)[b]
C_{14} hydro-phenanthrene	68476-31-3 68553-00-4 68476-33-5	255	21	4.5
C_{18} hydro-chrysene	68476-31-3 68553-00-4 68476-33-5	353 (expt.)	115 (expt.)	0.004
C_{22} hydropicene	68476-31-3 68553-00-4 68476-33-5	365	108	0.003

One-ring aromatics

Chemical name (CAS RN)	HFO represented	Boiling point (°C)	Melting point (°C)	Vapour pressure (Pa)[b]
C_{12} 1,2,3-triethyl benzene (42205-08-3)	68476-31-3 68553-00-4 68476-33-5	230	11.9	10.6
C_{15} 2-nonyl benzene (1081-77-2)	68476-31-3 68553-00-4 68476-33-5	281 (expt.)	-24 (expt.)	0.8 (expt.)
C_{20} tetradecyl benzene	68476-31-3 68553-00-4 68476-33-5	359 (expt.)	16 (expt.)	0.004 (expt.)

Chemical name (CAS RN)	HFO represented	Boiling point (°C)	Melting point (°C)	Vapour pressure (Pa)[b]
(1459-10-5)				
C_{20} 1-benzyl-4,8-dimethyl-dodecane	68476-31-3 68553-00-4 68476-33-5	334.6	49.2	0.02
C_{30} 1-benzyl 4,8,12,16 tetramethyl eicosane	68476-31-3 68553-00-4 68476-33-5	437	131	1.2×10^{-5}
C_{50}	68553-00-4	697	305	2×10^{-14}

Cycloalkane monoaromatics

Chemical name (CAS RN)	HFO represented	Boiling point (°C)	Melting point (°C)	Vapour pressure (Pa)[b]
C_{15} methyl-octahydro-phenanthrene	68476-31-3 68553-00-4 68476-33-5	267	28	2.3
C_{20} ethyl-dodecahydro-chyrsene	68476-31-3 68553-00-4 68476-33-5	338	82	0.02

Two-ring aromatics

Chemical name (CAS RN)	HFO represented	Boiling point (°C)	Melting point (°C)	Vapour pressure (Pa)[b]
C_{15} 4-isopropyl biphenyl (7116-95-2)	68476-31-3 68553-00-4 68476-33-5	309	44	0.1
C_{20} 2-isodecyl naphthalene	68476-31-3 68553-00-4 68476-33-5	366	99	0.001
C_{30} 2-(4,8,14,18-tetramethyl hexadecyl) naphthalene	68476-31-3 68553-00-4 68476-33-5	468	171	7×10^{-7}
C_{50}	68553-00-4	722	316	3×10^{-15}

Cycloalkane diaromatics

Chemical name (CAS RN)	HFO represented	Boiling point (°C)	Melting point (°C)	Vapour pressure (Pa)[b]
C_{12} acenaphthene (83-32-9)	68476-31-3 68553-00-4 68476-33-5	279 (expt.)	93.4 (expt.)	0.3 (expt.)
C_{15} ethylfluorene	68476-31-3 68553-00-4 68476-33-5	338	95	0.007
C_{20} isoheptyl fluorene	68476-31-3 68553-00-4 68476-33-5	381	126	0.0003

Three-ring aromatics

Chemical name (CAS RN)	HFO represented	Boiling point (°C)	Melting point (°C)	Vapour pressure (Pa)[b]
C_{15} 2-methyl phenanthrene (2531-84-2)	68476-31-3 68553-00-4 68476-33-5	155-160 (expt.)	57-59 (expt.)	0.009
C_{20} 2-isohexyl phenanthrene	68476-31-3 68553-00-4 68476-33-5	331	67	0.04
C_{30} 2-(2,4,10-trimethyl tridecyl) phenanthrene	68476-31-3 68553-00-4 68476-33-5	493	191.6	1×10^{-7}
C_{50}	68553-00-4	746	327.5	4.87×10^{-16}

Four-ring aromatics

Chemical name (CAS RN)	HFO represented	Boiling point (°C)	Melting point (°C)	Vapour pressure (Pa)[b]
C_{16} fluoranthene	68476-31-3 68553-00-4 68476-33-5	384 (expt.)	107.8 (expt.)	1×10^{-3} (expt.)
C_{20} Benzo[*k*]fluoranthene	68476-31-3 68553-00-4 68476-33-5	480 (expt.)	217 (expt.)	1×10^{-7} (expt.)

Five-ring PAHs

Chemical name (CAS RN)	HFO represented	Boiling point (°C)	Melting point (°C)	Vapour pressure (Pa)[b]
C_{20} benzo[*a*]pyrene (50-32-8)	68476-31-3 68553-00-4 68476-33-5	495 (expt.)	177 (expt.)	7×10^{-7}
C_{30} dimethyloctyl-benzo[*a*]pyrene	68476-31-3 68553-00-4 68476-33-5	545	231	2×10^{-9}

Six-ring aromatics

Chemical name (CAS RN)	HFO represented	Boiling point (°C)	Melting point (°C)	Vapour pressure (Pa)[b]
C_{22} Benzo[*ghi*] perylene 191-24-2	68476-31-3 68553-00-4 68476-33-5	More than 500 (expt.)	278 (expt.)	1×10^{-8} (expt.)

Table B-1 cont. Physical-chemical properties for representative structures of HFOs[a]

Alkanes

Chemical name (CAS RN)	Henry's Law constant ($Pa*m^3/mol$)[c]	Log K_{ow}	Log K_{oc}	Aqueous solubility (mg/L)[d]
C_{12} dodecane (112-40-3)	8.3×10^{5} (expt.)	6.1 (expt.)	5.3	0.004 (expt.)
C_{15} pentadecane (629-62-9)	1.3×10^{6} (expt.)	7.7	6.7	8×10^{-5} (expt.)
C_{20} eicosane (112-95-8)	2.2×10^{7}	10	8.8	0.02 (expt.)
C_{30} triacontane	6.8×10^{8}	15.1	13.0	8.6×10^{-11}
C_{50}	3.6×10^{10}	25	21.6	2.6×10^{-21}

Isoalkanes

Chemical name (CAS RN)	Henry's Law constant ($Pa*m^3/mol$)[c]	Log K_{ow}	Log K_{oc}	Aqueous solubility (mg/L)[d]
C_{12} 2,3-dimethyldecane (17312-44-6)	2×10^{6}	6.1	5.3	0.1
C_{15} 2-methyl tetradecane (1560-95-8)	4.6×10^{6}	7.6	6.6	0.003
C_{20} 3-methyl nonadecane (6418-45-7)	2.6×10^{7}	10.1	8.8	1×10^{-5}
C_{30} hexamethyl tetracosane (111-01-3)	2×10^{9}	14.6	12.7	2×10^{-10}
C_{50}	1.5×10^{10}	25	21.5	6×10^{-21}

One-ring cycloalkanes

Chemical name (CAS RN)	Henry's Law constant ($Pa*m^3/mol$)[c]	Log K_{ow}	Log K_{oc}	Aqueous solubility (mg/L)[d]
C_{12} *n*-heptylcyclo pentane	1.9×10^{5}	6.1	5.3	0.1
C_{15} nonylcyclo hexane (2883-02-5)	5.3×10^{5}	7.5	6.5	0.005
C_{20} tetradecyl cyclohexane (1795-18-2)	3×16^{9}	10.0	8.7	1.7×10^{-6}
C_{30} 1,5-dimethyl-1-(3,7,11,15-tetramethyl octadecyl) cyclohexane	2.9×10^{8}	14.5	12.5	4.2×10^{-7}
C_{50}	2×10^{11}	24.4	21.2	1.4×10^{-20}

Two-ring cycloalkanes

Chemical name (CAS RN)	Henry's Law constant ($Pa*m^3/mol$)[c]	Log K_{ow}	Log K_{oc}	Aqueous solubility (mg/L)[d]
C_{12} dicyclohexyl (92-51-3)	2.6×10^{4}	5.9	5.1	0.2
C_{15} pentamethyl decalin (91-17-8)	4.8×10^{4} (expt.)	4.2	3.7 (expt.)	0.9 (expt.)
C_{20} 2,4-dimethyloctyl-2-decalin	7.2×10^{5}	8.9	7.7	1.2×10^{-4}
C_{30} 2,4,6,10,14 pentamethyl dodecyl-2-decalin	3.9×10^{7}	13.6	11.8	1.7×10^{-9}
C_{50}	5.7×10^{10}	23.2	20.2	1.4×10^{-19}

Polycycloalkanes

Chemical name (CAS RN)	Henry's Law constant ($Pa*m^3/mol$)[c]	Log K_{ow}	Log K_{oc}	Aqueous solubility (mg/L)[d]
C_{14} hydrophenanthrene	8590	5.2	4.5	0.5
C_{18} hydro-chrysene	5680	6.2	5.4	0.01
C_{22} hydro-picene	3750	7.3	6.3	0.002

One-ring aromatics

Chemical name (CAS RN)	Henry's Law constant ($Pa*m^3/mol$)[c]	Log K_{ow}	Log K_{oc}	Aqueous solubility (mg/L)[d]
C_{12} 1,2,4-triethylbenzene (877-44-1)	2480	5.1	4.4	2.9
C_{15} 2-nonylbenzene (1081-77-2)	1×10^{4}	7.1 (expt.)	6.1	0.03
C_{20}	5.7×10^{4}	10	8.6	5×10^{-5}

Chemical name (CAS RN)	Henry's Law constant ($Pa*m^3/mol$)[c]	Log K_{ow}	Log K_{oc}	Aqueous solubility (mg/L)[d]
tetradecylbenzene		(expt.)		
C_{20} 1-benzyl-4,8-dimethyl-dodecane	8.2×10^4	8.8	7.6	5.5×10^{-4}
C_{30} 1-benzyl 4,8,12,16 tetramethyl eicosane	3.8×10^6	13.5	12.0	7×10^{-9}
C_{50}	1×10^9	23.8	21.0	2×10^{-19}

Cycloalkane monoaromatics

Chemical name (CAS RN)	Henry's Law constant ($Pa*m^3/mol$)[c]	Log K_{ow}	Log K_{oc}	Aqueous solubility (mg/L)[d]
C_{15} methyloctahydro-phenanthrene	1.5×10^4	5.6	4.9	0.2
C_{20} ethyldodecahydro-chyrsene	1.4×10^4	7.1	6.2	0.004

Two-ring aromatics

Chemical name (CAS RN)	Henry's Law constant ($Pa*m^3/mol$)[c]	Log K_{ow}	Log K_{oc}	Aqueous solubility (mg/L)[d]
C_{15} 4-isopropyl biphenyl	98.7	5.5 (expt.)	4.8	0.9
C_{20} 2-isodecyl naphthalene	1190	8.1	7.0	0.002
C_{30} 2-(4,8,14,18-tetramethyl hexadecyl) naphthalene	5.4×10^4	12.8	11.1	3×10^{-8}
C_{50}	8.6×10^6	23.2	20.2	7×10^{-19}

Cycloalkane diaromatics

Chemical name (CAS RN)	Henry's Law constant ($Pa*m^3/mol$)[c]	Log K_{ow}	Log K_{oc}	Aqueous solubility (mg/L)[d]
C_{12} acenaphthene (83-32-9)	18.6 (expt.)	3.9 (expt.)	3.6 (expt.)	3.9 (expt.)
C_{15} ethylfluorene	5.6	5.1	4.4	0.2
C_{20} isoheptylfluorene	32.7	7.5	6.5	0.0006

Three-ring aromatics

Chemical name (CAS RN)	Henry's Law constant ($Pa*m^3/mol$)[c]	Log K_{ow}	Log K_{oc}	Aqueous solubility (mg/L)[d]
C_{15} 2-methyl phenanthrene (2531-84-2)	2.8	4.9 (expt.)	4.2	0.3 (expt.)
C_{20} 2-isohexyl phenanthrene	9.9×10^{4}	8.0	7.0	7×10^{-4}
C_{30} 2-(2,4,10-trimethyltridecyl) phenanthrene	942	12	10	1×10^{-8}
C_{50}	3.1×10^{5}	23.0	19.3	3.5×10^{-19}

Four-ring aromatics

Chemical name (CAS RN)	Henry's Law constant ($Pa*m^3/mol$)[c]	Log K_{ow}	Log K_{oc}	Aqueous solubility (mg/L)[d]
C_{16} fluoranthene (206-44-0)	0.9 (expt.)	5.2 (expt.)	4.8 (expt.)	0.26 (expt.)
C_{20} benzo[*k*]fluoranthene	0.06 (expt.)	6.1 (expt.)	5.6 (expt.)	0.0008 (expt.)

Five-ring PAHs

Chemical name (CAS RN)	Henry's Law constant ($Pa*m^3/mol$)[c]	Log K_{ow}	Log K_{oc}	Aqueous solubility (mg/L)[d]
C_{20} benzo[*a*]pyrene (50-32-8)	0.05 (expt.)	6.1 (expt.)	6.0 (expt.)	0.002 (expt.)
C_{30} dimethyloctyl-benzo[*a*]pyrene	0.8	10.9	9.5	1×10^{-7}

Six-ring aromatics

Chemical name (CAS RN)	Henry's Law constant ($Pa*m^3/mol$)[c]	Log K_{ow}	Log K_{oc}	Aqueous solubility (mg/L)[d]
C_{22} benzo[*ghi*]perylene (191-24-2)	0.03 (expt.)	6.6 (expt.)	5.8	0.0003 (expt.)

[a] All values are modelled unless denoted with an (expt.) for experimental data.
[b] This is the maximum vapour pressure of the representative structure; the actual vapour pressure as a component of a mixture will be lower due to Raoult's Law (the total vapour pressure of an ideal mixture is proportional to the sum of the vapour pressures of the mole fractions of each individual component). The lightest C_{12} and heaviest C_{50} representative structures were chosen to estimate a range of vapour pressures from the minimum to maximum values.
[c] Henry's Law constants for C_{20}–C_{30} representative structures were calculated with HENRYWIN Version 3.10 from EPI Suite (2008), using both sub-cooled liquid solubility and sub-cooled liquid vapour pressure. Henry's Law constants for C_{50} representative structures were not calculated, as sub-cooled liquid solubility data were not available. Solubility data gave anomalously high values for substances that have negligible solubility and volatility.
[d] Maximum water solubility was estimated for each representative structure based on its individual physical-chemical properties. The actual water solubility of a component in a mixture will be lower, as the total water solubility of an ideal mixture is proportional to the sum of the water solubilities of the mole fractions of each individual component (Banerjee 1984).

Appendix C: Production and Transportation of Fuel Oil No. 6, Fuel Oil No. 4 and Residual Fuel Oil

Table C-1a. Supply and disposition of HFOs[a] in Canada in thousands of cubic metres, 2008 (Statistics Canada 2009)

-	Alberta	Ontario	Quebec	Atlantic	Other provinces and territories	Canada
Refinery production	790.0	673.7	2681.5	3788.4	324.2	8257.6[b]
Imports	0.0	60.8	316.0	869.6	521.0	1767.4
Exports	215.2	75.3	1347.0	2784.4	128.0	4549.8[b]
Domestic sales	47.5	699.2	2872.2	1502.1	1275.4	6396.4

[a] Fuel Oil No. 4, Fuel Oil No. 5, Fuel Oil No. 6 and low-sulphur types for both steam and diesel engines.
[b] Totals may not add up due to rounding.

Table C-1b. HFO[a] production and imports available for sale in Canada in thousands of cubic metres, 2006–2008 (Environment Canada 2008, 2009, 2010)

Regions	2006	2007	2008[b]
Atlantic region	1849	2261	1663
Quebec	2491	2802	2871
Ontario	1285	1228	841
West region	1086	1275	1257
Canada	**6711**	**7567[c]**	**6632**

[a] Fuel Oil No. 4, Fuel Oil No. 5, Fuel Oil No. 6 and low-sulphur types for both steam and diesel engines.
[b] Variances between data from Environment Canada 2010 and Statistics Canada 2009 (Table C-1a in Appendix C) may be a result of differences in approach used to determine volumes. For example, volumes reported to Environment Canada mostly reflect production at various refineries, while Statistics Canada considers opening and closing inventories and inter-product transfers (Environment Canada 2010).
[c] Totals may not add up due to rounding.

Table C-1c. Production and movement of Fuel Oil No. 4, Fuel Oil No. 5 and Fuel Oil No. 6 in Canada in thousands of cubic metres, 2004–2008 (Statistics Canada 2005–2009)

	Refinery production	Imports	Exports
2004	9154	2919	3678
2005	8670	2740	3668
2006	8146	1563	3714
2007	8617	1938	4317
2008	8258	1767	4550

[a] Fuel Oil No. 4, Fuel Oil No. 5, Fuel Oil No. 6 and low-sulphur types for both steam and diesel engines.

Table C-2. Disposition of HFOs[a] in Canada, 2008 (Statistics Canada 2010)

Application	Thousands of cubic metres	Share (%)
Producer consumption	503.1	7.1
Electricity by utilities	1115.6	15.8
Electricity by industry	81.2	1.2
Steam generation	49.8	0.7
Stock change, utilities and industry	1087.5	15.4
Non-energy use	0.0	0.0
Other energy use (energy production)	4 237.4	59.9
Total demand	**7074.6**	**100.0**

Table C-3. Sector consumption of HFOs[a] in Canada, 2008 (Statistics Canada 2010)

Sector	Thousands of cubic metres	Share (%)
Manufacturing	1231.8	28.97
Marine transportation	1538.2	36.17
Commercial/institutional	1013.2	23.83
Mining and oil and gas extraction	246.0	5.79
Public administration	100.3	2.36
Agriculture	76.2	1.79
Forestry, logging, and support	26.7	0.63
Construction	3.0	0.07

Residential[b]	16.9	0.40
Total	**4252.3**	**100**

[a] Fuel Oil No. 4, Fuel Oil No. 5, Fuel Oil No. 6 and low-sulphur types for both steam and diesel engines.
[b] This application is expected to involve the use of HFOs in large, multi-unit residential heating systems (furnace or boiler).
Note: There is a small statistical discrepancy between the reported total energy uses of HFOs above (4252.3 megalitres) and the 4237.4 megalitres shown in Table C-2 in Appendix C.

Table C-4. Reported and extrapolated release volumes and spill numbers of Bunker C spilled in Canada, 2000–2009 (Environment Canada 2011a)

Year	Average spill volume (litres)	Maximum single spill volume (litres)	Median spill volume (litres)	Number of spills reported	% of spills with unknown volume	Total known volume spilled (litres)	Extrapolated total volume spilled[a] (litres)
2009	12 592	98 000	636	16	43.8	113 330	162 834
2008	21 101	196 000	75	15	26.7	232 115	260 404
2007	27 000	222 460	200	27	22.2	566 995	609 428
2006	1 197	15 000	261	32	25	28 726	85 303
2005[b]	6 351	127 184	227	52	36.5	209 599	343 969
2004	7 523	98 000	182	39	30.8	203 131	287 997
2003	4 230	79 490	132	43	34.9	118 438	224 520
2002	2 325	60 000	227	58	27.6	97 662	210 815
2001	3 182	65 000	216	32	18.8	82 744	125 177
2000	2 083	27 822	95	25	28.0	37 491	86 995
-	-	-	-	-	**Total volume spilled**	**1 690 232**	**2 397 441**

[a] The extrapolated total volume was calculated using a proportional estimate of known spills to determine the frequency and volume of unknown spill volumes, assuming that the distribution of reported volumes released was representative of all releases.
[b] Does not include the 734 000 L spill in 2005 at Lake Wabamun, Alberta.

Table C-5. Approximate volume (litres) of Bunker C spills in Canada, 2000–2009 (Environment Canada 2011a)

Province	2000	2001	2002	2003	2004
Alberta	NA	NA	NA	NA	NA
British Columbia	20	4 396	4 782	3 951	15
Ontario	NA	65 000	900	2 270	35 000
Quebec	2 520	3 370	62 155	19 970	160 351
New Brunswick	5 784	5 700	19 939	9 165	792
Nova Scotia	28 438	3 528	3 484	345	105
Prince Edward Island	NA	14	2	568	NA
Newfoundland and Labrador	729	736	6 430	82 169	2 868
Nunavut	NA	NA	NA	NA	NA
Northwest Territories	NA	NA	NA	NA	4000
Yearly[b] total	**37 491**	**82 744**	**15 598**	**16 299**	**203 131**

Table C-5 cont. Approximate volume (litres) of Bunker C spills in Canada, 2000–2009 (Environment Canada 2011a)

Province	2005	2006	2007	2008	2009	Total
Alberta	NA[a]	NA	NA	NA	NA	NA
British Columbia	8 259	76	NA	NA	NA	21 499
Ontario	25 185	1 200	NA	NA	5 200	134 755
Quebec	1 277	16 552	433 728	223 449	NA	923 372
New Brunswick	15 717	733	89	8 586	2 293	68 798
Nova Scotia	141 171	5 684	129 273	81	98 836	410 915
Prince Edward Island	5000	NA	1 095	NA	NA	6 678
Newfoundland and Labrador	12 991	4 182	2 787	NA	7001	119 893
Nunavut	NA	300	NA	NA	NA	300
Northwest Territories	NA	NA	NA	NA	NA	4 000
Yearly total[b]	**209 600**	**28 727**	**566 972**	**232 116**	**113 330**	-

NA – no reported spill volumes.

[a] Does not include the 734 000 L spill in 2005 at Lake Wabamun, Alberta.

[b] Some spills in the NEMISIS database did not specify in which province they were spilled and were therefore not included in this table.

Table C-6. Number of Bunker C spills[a] affecting air, land, freshwater and saltwater in Canada,2000–2009 (Environment Canada 2011a)

	Air	Land	Freshwater	Saltwater	Total
2000	0	10	1	8	19
2001	1	12	4	11	27
2002	1	21	6	20	47
2003	1	15	7	12	34
2004	0	10	7	15	32
2005	0	22	10	17	49
2006	0	21	5	7	33
2007	0	9	8	7	24
2008	0	7	4	5	16
2009	1	4	3	6	13
Total	**4**	**131**	**55**	**108**	-

[a] Does not include the 734 000 L spill in 2005 at Lake Wabamun, Alberta.

Table C-7a. Sources of Bunker C spills in Canada, 2000–2009 (Environment Canada 2011a)

Source	Total number of releases	Total volume of releases (litres)	Proportion of volume	Average release (litres)
Other watercraft	43	416 759	0.25	14 371
Pipeline	13	333 431	0.20	33 343
Marine tanker	9	323 523	0.19	40 440
Other	46	156 374	0.09	4 739
Other industrial plant	44	133 540	0.08	3 257
Marine terminal	16	132 093	0.08	12 008
Train	11	61 304	0.04	10 217
Tank truck	21	37 431	0.02	2 202
Refinery	23	31 904	0.02	1 679
Other storage facilities	22	28 945	0.02	1 809
Unknown	36	9 294	0.01	774
Storage depot	7	6 550	0.00	936
Transport truck	5	5 150	0.00	1 030
Barge	8	5 018	0.00	1 004
Bulk carrier	12	3 805	0.00	951
Chemical plant	2	2 270	0.00	2 270
Electrical equipment	7	1 274	0.00	182
Other motor vehicle	6	1 129	0.00	282
Production field	4	418	0.00	139
Migration	2	20	0.00	20

Source	Total number of releases	Total volume of releases (litres)	Proportion of volume	Average release (litres)
Municipal sewer	1	0	0.00	0
Service station	1	0	0.00	0
Aircraft	0	0	0.00	0
Municipal sewage treatment plant	0	0	0.00	0
Total	**339**	**1 690 232**	**1.00**	**7 072**

Table C-7b. Causes of Bunker C spills in Canada, 2000–2009 (Environment Canada 2011a)

Cause	Total number of releases	Total volume of releases (litres)	Proportion of volume	Average release (litres)
Pipe leak	74	644 515	0.38	10 742
Unknown	72	414 993	0.25	11 216
Sinking	5	222 860	0.13	111 430
Other	47	141 964	0.08	4 302
Grounding	7	98 980	0.06	32 993
Overflow	35	61 692	0.04	2 056
Above-ground tank leak	19	51 597	0.03	3 440
Valve, fitting leak	23	16 600	0.01	755
Container leak	21	11 267	0.01	751
Discharge	18	10 174	0.01	1 130
Overturn	6	6 637	0.00	1 659
Process upset	3	4 928	0.00	1 643
Underground tank leak	2	2 880	0.00	2 880
Well blowout	2	500	0.00	250
Cooling system leak	2	443	0.00	221
Derailment	3	200	0.00	200
Total	**339**	**1 690 232**	**1.00**	**7 072**

Table C-7c. Reasons for Bunker C spills in Canada, 2000–2009 (Environment Canada 2011a)

Reason	Total number of releases	Total volume of releases (litres)	Proportion of volume	Average release (litres)
Unknown	119	721 969	0.43	10 617

Material failure	42	270 403	0.16	7 726
Human error	56	263 605	0.16	5 380
Other	29	196 316	0.12	10 332
Fire, explosion	1	98 000	0.06	98 000
Equipment failure	65	77 178	0.05	1 642
Negligence	3	35 000	0.02	35 000
Gasket, joint	11	19 011	0.01	1 728
Damage by equipment	4	5 520	0.00	1 840
Power failure	2	2 270	0.00	2 270
Corrosion	2	569	0.00	569
Weld, seam failure	1	190	0.00	190
Intent	2	182	0.00	182
Migration	2	20	0.00	20
Overstress	0	0	0.00	0
Total	**339**	**1 690 232**	**1.00**	**7 072**

Appendix D: Environmental Fate Processes Affecting HFOs

Table D-1. Changes in the concentration (wt %) of Heavy Fuel Oil 6303 (Bunker C; representing Fuel Oil No. 6) components after weathering (Environment Canada 2010a)

Component	0% weathered	2.5% weathered
Alkanes (saturates)	42.5	38.8
Aromatics	29.0	26.9
Resins	15.5	16.6
Asphaltenes	13.0	17.7
Waxes	2.5	2.7

Table D-2. Changes in the concentration (µg/g) of volatile organic compounds in Heavy Fuel Oil 6303 (Bunker C; representing Fuel Oil No. 6) after weathering (Environment Canada 2010)

Volatile Organic Compound	0% weathered	2.5% weathered
Benzene	40	0
Toluene	136	0
Ethylbenzene	58	0
Xylenes	396	0
C_3-benzenes	940	50
Total BTEX	**630**	**0**
Total BTEX and C_3-benzenes	**1570**	**50**

Appendix E: Persistence and Bioaccumulation

Table E-1. An analysis of persistence data for petroleum hydrocarbons representative of Fuel Oil No. 4, Fuel Oil No. 6 and Residual Fuel Oil based on Environment Canada (2014).

# of carbons	C_{12}	C_{13}	C_{14}	C_{15}	C_{18}	C_{20}	C_{22}	C_{30}	C_{50}
***n*-alkane**	n/a	n/a	n/a	-	-	-	n/a	-	-
***i*-alkane**	-	-	n/a	-	n/a	-	n/a	S,W, Sd	-
monocyclo-alkane	-	n/a	n/a	-	n/a	-	n/a	Sd	S,W, Sd
dicyclo-alkane	Sd	n/a	n/a	S,W, Sd	n/a	S,W, Sd	n/a	S,W, Sd	S,W, Sd
Polycyclo-alkane	n/a	n/a	Sd	n/a	S,W, Sd	n/a	S,W, Sd	n/a	n/a
mono-aromatic	S, W, Sd	n/a	n/a	Sd	n/a	-	n/a	Sd	Sd
Cycloalkane mono-aromatic	S, W, Sd	n/a	n/a	S,W, Sd	n/a	S,W, Sd	n/a	n/a	n/a
diaromatic	S, W, Sd	n/a	n/a	S,W, Sd	n/a	S,W, Sd	n/a	S,W, Sd	S,W, Sd
Cycloalkane diaromatic	S, W, Sd	A	n/a	-	n/a	-	n/a	n/a	n/a
3-ring polyaromatic	A	n/a	A, S,W ,Sd	-	n/a	-	n/a	S,W, Sd	S,W, Sd
4-ring polyaromatic	n/a	n/a	n/a	n/a	A, S,W, Sd	S,W, Sd	n/a	n/a	n/a
5-ring polyaromatic	n/a	n/a	n/a	n/a	n/a	A, S,W, Sd	n/a	S,W, Sd	n/a
6-ring polyaromatic	n/a	n/a	n/a	n/a	n/a	n/a	A, S,W, Sd	n/a	n/a

A – Predicted half-life in air of 2 days or greater
S – Predicted half-lives in soil of 6 months or greater
W – Predicted half-lives in water of 6 months or greater
Sd – Predicted half-life in sediment of one year or greater
n/a – not-applicable. Indicates that no such carbon number exists within the group or it was not modelled

- Indicates that these structures are not considered to persist for long periods of time in air, soil, water, or sediment.

Table E-2. An analysis of experimental and modelled bioaccumulation data for petroleum hydrocarbons representative of Fuel Oil No. 4, Fuel Oil No. 6 and Residual Fuel Oil based on Environment Canada (2014).

# of carbons[a]	C_{12}	C_{13}	C_{14}	C_{15}	C_{18}	C_{20}	C_{22}	C_{25}
n-alkane	-	-	-	-	-	-	n/a	n/a
i-alkane	-	B	n/a	B	n/a	n/a	n/a	n/a
mono-cycloalkane	B	n/a	n/a	B	n/a	n/a	n/a	n/a
dicycloalkane	B	-	n/a	B	n/a	n/a	n/a	n/a
poly-cycloalkane	n/a	n/a	B	n/a	-	n/a	B	n/a
monoaromatic	-	n/a	n/a	B	n/a	n/a	n/a	n/a
Cycloalkane monoaromatic	-	n/a	n/a	B	n/a	B	n/a	n/a
Diaromatic	B	B	-	-	n/a	n/a	n/a	n/a
Cycloalkane diaromatic	-	-	-	-	n/a	B	n/a	n/a
3-ring polyaromatic	-	n/a	B	-	n/a	B	n/a	n/a
4-ring poly-aromatic	n/a	n/a	n/a	B	B	B	n/a	n/a
5-ring poly-aromatic	n/a	n/a	n/a	n/a	n/a	B	B	n/a
6-ring poly-aromatic	n/a	n/a	n/a	n/a	n/a	n/a	B	n/a

[a]Structures with carbon number >C_{25} are not expected to bioaccumulate.
B – Predicted highly bioaccumulative with a BCF/BAF greater than 5000
n/a – not-applicable. Indicates that no such carbon number exists within the group or it was not modelled
- Indicates that these structures are not considered highly bioaccumulative.

Appendix F: Ecotoxicological Information

Table F-1a. Aquatic toxicity of Fuel Oil No. 6

Fish

Test organism (common name)	Type of test	Comment	Value (mg/L)	Reference
Oncorhynchus kisutch (coho salmon)	96-hr acute LC_{50}	OWD	4800	Hebert and Kussat 1972
Oncorhynchus kisutch (coho salmon)	96-hr acute LC_{50}	OWD	> 10 000	Hebert and Kussat 1972
Oncorhynchus kisutch (coho salmon)	96-hr acute LC_{50}	OWD	7500	Hebert and Kussat 1972
Alosa sapidissma (American shad)	48-hr acute LC_{50}	Not reported	2417	Tagatz 1961
Leptocottus armatus (staghorn sculpin)	96-hr acute LC_{50}	OWD	780	Hebert and Kussat 1972
Leptocottus armatus (staghorn sculpin)	96-hr acute LC_{50}	OWD	5600	Hebert and Kussat 1972
Leptocottus armatus (staghorn sculpin)	96-hr acute LC_{50}	OWD	3400	Hebert and Kussat 1972
Salmo salar (Atlantic salmon)	96-hr acute LC_{50}	OWD	> 10 000	Sprague and Carson 1970
Pseudopleuronectes americanus (winter flounder)	96-hr acute LC_{50}	OWD	> 10 000	Sprague and Carson 1970
Fundulus similis (longnose killifish)	24-hr acute LC_{50}	WSF[a]	3.8	Anderson et al. 1974
Fundulus similis (longnose killifish)	48-hr acute LC_{50}	WSF[a]	2.27	Anderson et al. 1974
Fundulus similis (longnose killifish)	96-hr acute LC_{50}	WSF[a]	1.69	Anderson et al. 1974
Menidia menidia (Atlantic silverside)	96-hr acute LC_{50}	Not reported	130	Hollister et al. 1980
Cyprinodon variegates (sheepshead minnow)	96-hr acute LC_{50}	WSF[a]	4.7	Anderson et al. 1974
Cyprinodon variegatus	96-hr acute LC_{50}	WSF[a]	4.4	Anderson et al. 1974

Test organism (common name)	Type of test	Comment	Value (mg/L)	Reference
(sheepshead minnow)				
Cyprinodon variegatus (sheepshead minnow)	96-hr acute LC_{50}	WSF[a]	3.1	Anderson et al. 1974
Menidia beryllina (inland silverside)	24-hr acute LC_{50}	WSF[a]	3.6	Anderson et al. 1974
Menidia beryllina (inland silverside)	48-hr acute LC_{50}	WSF[a]	2.7	Anderson et al. 1974
Menidia beryllina (inland silverside)	96-hr acute LC_{50}	WSF[a]	1.9	Anderson et al. 1974
Lepomis macrochirus (bluegill)	96-hr acute LC_{50}	OWD	> 10 000	Mobil 1987a

Invertebrates

Test organism (common name)	Type of test	Comment	Value (mg/L)	Reference
Daphnia magna (water flea)	48-hr acute EC_{50} (immobilization)	WSF	4.14	MacLean and Doe 1989
Daphnia magna (water flea)	48-hr acute LC_{50}	WSF	> 4.45	MacLean and Doe 1989
Daphnia magna (water flea)	48-hr acute EL_{50}	OWD	> 10 000	Mobil 1987b
Artemia salina (brine shrimp)	48-hr acute EC_{50} (immobilization)	WSF	> 2.29	MacLean and Doe 1989
Artemia salina (brine shrimp)	48-hr acute LC_{50}	WSF	> 2.29	MacLean and Doe 1989
Acartia tonsa (copepod)	96-hr acute LC_{50}	Not reported	5.1	Hollister et al. 1980
Paleomonetes pugio (grass shrimp)	24-hr acute LD_{50}	WSF[a]	3.2	Anderson et al. 1974
Paleomonetes pugio (grass shrimp)	48-hr acute LD_{50}	WSF[a]	2.8	Anderson et al. 1974
Paleomonetes pugio (grass shrimp)	96-hr acute LD_{50}	WSF[a]	2.6	Anderson et al. 1974
Paleomonetes pugio (grass shrimp)	96-hr acute LC_{50}	WSF-1:9, 20-hr mix, serial dilutions, ppm	2.6 3.1 2.2	Tatem et al. 1978

Test organism (common name)	Type of test	Comment	Value (mg/L)	Reference
		dissolved total HC by IR		
Penaeus aztecus (postlarvae) (brown shrimp)	24-hr acute LC_{50}	WSF[a]	3.8	Anderson et al. 1974
Penaeus aztecus (postlarvae) (brown shrimp)	48-hr acute LC_{50}	WSF[a]	3.5	Anderson et al. 1974
Penaeus aztecus (postlarvae) (brown shrimp)	96-hr acute LC_{50}	WSF[a]	1.9	Anderson et al. 1974
Limulus polyphemus (horseshoe crabs [juvenile])	7 days (Increased mortality and delayed moult)		2.25	Strobel and Brenowitz 1981
Mercenaria mercenaria (horseshoe crabs [juvenile])	48-hr acute LC_{50}	WSF concentration = 25.2 ± 1.7 ppm	1.0 (0.7–1.6) ppm	Byrne and Calder 1977
Mercenaria mercenaria (horseshoe crabs [juvenile])	48-hr acute LC_{50}	WSF concentration = 25.2 ± 1.7 ppm	3.2 (2.3–4.5) ppm	Byrne and Calder 1977
Mercenaria mercenaria (horseshoe crabs [juvenile])	6-day LC_{50}	WSF concentration = 25.2 ± 1.7 ppm	1.8 (1.0–2.6) ppm	Byrne and Calder 1977
Mercenaria mercenaria (horseshoe crabs [juvenile])	10-day LC_{50}	WSF concentration = 25.2 ± 1.7 ppm	1.6 (1.1–2.2) ppm	Byrne and Calder 1977
Mercenaria mercenaria (horseshoe crabs [juvenile])	6-day growth test EC_{50}	WSF concentration = 25.2 ± 1.7 ppm	1.9 (1.6–2.1) ppm	Byrne and Calder 1977
Mercenaria mercenaria (horseshoe crabs [juvenile])	10-day growth test EC_{50}	WSF concentration = 25.2 ± 1.7 ppm	1.0 (0.49–2.04) ppm	Byrne and Calder 1977
Neanthes arenaceodentata (polychaete marine	96-hr acute LC_{50}	Not given	3.6	Neff and Anderson 1981

Test organism (common name)	Type of test	Comment	Value (mg/L)	Reference
worm)				
Neanthes arenaceodentata (polychaete marine worm)	24-hr acute LC_{50}	WSF	> 6.3	Rossi et al. 1976
Neanthes arenaceodentata (polychaete marine worm)	48-hr acute LC_{50}	WSF	4.6	Rossi et al. 1976
Neanthes arenaceodentata (polychaete marine worm)	96-hr acute LC_{50}	WSF	3.6	Rossi et al. 1976
Capitella capitata (marine worm)	24-hr acute LC_{50}	WSF	> 6.3	Rossi et al. 1976
Capitella capitata (marine worm)	48-hr acute LC_{50}	WSF	1.1	Rossi et al. 1976
Capitella capitata (marine worm)	96-hr acute LC_{50}	WSF	0.9	Rossi et al. 1976
Capitella capitata (marine worm)	96-hr acute LC_{50}	Not reported	0.9	Neff and Anderson 1981
Mysidopsis almyra (mysid shrimp)	24-hr acute LC_{50}	WSF	6.3	Anderson et al. 1974

Algae

Test organism (common name)	Type of test	Comment	Value (mg/L)	Reference
Skeletonema costatum (diatom)	96-hr acute EC_{50}	Not given	160	Hollister et al. 1980
Pseudokirchneriella subcapitata (Selenastrum capricornutum) (green alga)	EC_{50}	WSF-1:8, 16-hour mix, serial dilutions	No inhibition – 100% WSF Stimulation – 0.1% WSF	Giddings et al. 1980
(Green alga)	96-hr acute EC_{50}	Material heated, spread in container, water overlay	> 5000	Mobil 1987c
Microsystus	EC_{50}	WSF-1:8,	No	Giddings et

Test organism (common name)	Type of test	Comment	Value (mg/L)	Reference
aeruginosa (blue-green alga)		16-hour mix, serial dilutions	inhibition – 100% WSF Stimulation – 0.1% WSF	al. 1980

Definitions:
LC_{50}: the concentration of a substance that is estimated to be lethal to 50% of the test organisms.
EC_{50}: the concentration of a substance that is estimated to cause a defined effect on 50% of the test organisms.
WSF: water-soluble fraction.
OWD: oil in water dispersion.
EL_{50}: the loading concentration of a substance that is estimated to cause some toxic effect on 50% of the test organisms.
[a] WSF-1:8, 20-hour mix, serial dilutions, LC_{50} based on ppm dissolved total hydrocarbons by IR.

Table F-1b. Aquatic toxicity of light and heavy Residual Fuel Oil (CAS RN 68476-33-5)

Test organism / common name	Residual Fuel Oil type	Type of test / endpoint	Comment	Value (mg/L)	Reference
Oncorhynchus mykiss rainbow trout	Heavy	96-hr acute LL_{50}	WAF; semistatic	100–1000	Shell 1997a
Oncorhynchus mykiss rainbow trout	Light	96-hr acute LL_{50}	WAF	More than 1000	Shell 1997b
Daphnia magna water flea	Heavy	48-hr acute EL_{50} (immobilization) NOEL	WAF; static	220–460 100 (10% immobilization)	Shell 1997c
Daphnia magna water flea	Light	48-hr acute EL_{50} (immobilization)	WAF	More than 1000	Shell 1997d
Raphidocelis subcapitata algae	Heavy	96-hr acute EL_{50} (growth rate)	WAF	30–100	Shell 1997e
	Light	72-hr acute EL_{50} (growth rate)	WAF	100–300	Shell 1997f

Definitions:
LL_{50}: the loading concentration of a substance that is estimated to be lethal to 50% of the test organisms.
EL_{50}: the loading concentration of a substance that is estimated to cause some toxic effect on 50% of the test organisms.

Table F-2. Acute systemic toxicity data for Fuel Oil No. 6 (CONCAWE 1998)

	Oral LD_{50}, rat (mg/kg)	Reference
Fuel Oil No. 6, API 78-6	> 25 000	API 1980b
Fuel Oil No. 6, API 78-7	> 25 000	API 1980a
Fuel Oil No. 6, API 78-8	> 24 700	API 1980c
Fuel Oil No. 6, API 79-2	5 130	API 1980d

Table F-3. Estimated volume of water in contact with high persistence oil ($m^3 \times 10^6$) for loading/unloading and transport processes of oil via ship for various spill sizes (RMRI 2007)

Spill size (barrels)	Loading/unloading	Transport
1–49	60	5 750
50–999	150	6 250
1000–9999	300	9 600
10 000–99 999	2 200	17 350
100 000–199 999	32 500	49 500
> 200 000	35 000	74 100

Appendix G: Summary of Health Effects Information for Fuel Oil No. 4, Fuel Oil No. 6, Residual Fuel Oil and Related HFOs

Endpoints	CAS RN[a]	Effect levels[b]/results
Acute health effects	**68476-33-5**	Inhalation LC_{50} (rat) = 4100 mg/m^3 (male and female). Non-lethal effects included laboured breathing, gasping and reduced activity (Bio/Dynamics Inc. 1987).
	64742-90-1	Lowest inhalation LC_{50} (rat) = > 3700 mg/m^3 (male and female) (U.S. EPA 2005).
	68553-00-4	Oral LD_{50}s (rat) = 5130, > 24 700, > 25 000 and > 25 000 mg/kg-bw (5.13, > 25, > 25 and > 25 mL/kg) for samples API 79-2, 78-8, 78-7 and 78-6, respectively (male and female) (CONCAWE 1998; API 2004; European Commission c2000b).
	64741-62-4	Lowest oral LD_{50} (rat) = > 2000 mg/kg-bw (male and female) (CONCAWE 1998; European Commission c2000b).
	64741-62-4 64741-45-3 64741-57-7 64741-81-7 64742-90-1	Other oral LD_{50}s (rat) = 4320–5898 mg/kg-bw for 5 CAS RNs tested (female and/or male) (CONCAWE 1998; API 2004; European Commission c2000b; U.S. EPA 2005).
	68476-31-3	Dermal LD_{50} (mouse) = > 40 000 mg/kg-bw (male and female) (CONCAWE 1996).
	68553-00-4	Dermal LD_{50}s (rabbit) = > 5350, > 5000, > 5000, > 4940 mg/kg-bw (> 5 mL/kg-bw) for samples API 79-2, 78-8, 78-7, 78-6, respectively (male and female) (CONCAWE 1998; API 2004; European Commission c2000b).
	64741-45-3 64741-57-7 64741-62-4 64741-81-7	Lowest dermal LD_{50} (rabbit) = > 2000 mg/kg-bw for 4 CAS RNs tested (male and female) (API 2004; CONCAWE 1998; European Commission c2000b).
	64742-90-1	Other dermal LD_{50} (rabbit) = > 3160 mg/kg-bw (male and female) (European Commission c2000b).
	64741-62-4	Other dermal LD_{50} (rat) = > 2000 mg/kg-bw (male and female) (European Commission c2000b).
Short-term, subchronic and and non-cancer chronic repeated-exposure health effects	**68476-31-3**	Inhalation LOAEC = ≤ 300 mg/m^3 for decreased body weight gain. Male and female rats were exposed for 90 days to 50 or 300 mg/m^3 test substance. Reduced body weight gain was observed at an unspecified concentration. Nephropathy was also observed in males, but was not considered by the authors to be relevant to humans (Cowan and Jenkins 1981).
	64742-90-1	Other inhalation study: Male and female Fischer 344 rats (5 animals per sex per concentration) were exposed to 540 or 2000 mg/m^3 test substance for 6 hours per day for 9 days. Concentration- and time-related decreases in body weight (greater effect in males), as well as concentration-related increases

Endpoints	CAS RN[a]	Effect levels[b]/results
		in hair loss, nasal discharge, discharge from the eyes, eyes closed and perianal soiling, were observed. Yellow discolouration of the lungs and hyperplasia of the pulmonary alveolar macrophages were also observed at all concentrations. Increased liver weight was observed in females at 540 mg/m^3 and in both sexes at 2000 mg/m^3. Increased lung (females), decreased spleen (male and female) and decreased heart (male) weights were also observed at the highest concentration (Gordon 1983).
	68476-31-3	Dermal study: Doses of 2000, 4000, 8000, 20 000 or 40 000 mg/kg-bw per day were applied to the clipped dorsal interscapular skin of male and female B6C3F$_1$ mice (5 animals per sex per dose) for 14 consecutive days. Skin lesions characterized by moderate acanthosis, perakeratosis and hyperkeratosis, accompanied by moderate mixed cellular inflammatory infiltrate within the upper dermis were observed at all doses. Mortality of all mice occurred between days 7 and 12 at the highest dose (NTP 1986). Dermal study: Doses of 425, 818 or 1625 mg/kg-bw per day (11.9, 22.9 or 45.5 mg per day)[c,d] were applied to male and female C3Hf mice, 3 days per week for 40 weeks. Decreased body weight (4–21%), increased spleen weight (male and female), increased relative kidney weight (females) and decreased relative kidney weight (males) were observed at 818 mg/kg-bw per day (Schultz et al. 1981). Dermal study: Doses of 694 or 1111 mg/kg-bw per day (50 µL of 50% w/v diluted in cyclohexane or 50 µL neat)[c,e,f] were applied to the clipped interscapular skin of male and female C3Hf/Bd mice (15 animals per sex per dose), 3 times per week for 60 weeks. Hyperkeratosis, alopecia and ulceration at the application site, as well as increased daily water consumption (possibly due to increased water loss) and increased urine output, were observed at all doses. An increased incidence of macroscopic renal lesions (affected kidneys were shrunken, pale and nodular) were observed in females at the highest dose (Easley et al. 1982). Dermal study: Doses of 250, 500, 1000 and 2000 mg/kg-bw per day (diluted in 0.2 mL of acetone) or 4000 mg/kg-bw per day (neat) were applied to the shaved interscapular skin of male and female B6C3F$_1$ mice (10 animals per sex per dose), 5 days per week for 13 weeks. Decreased body weight (8–13%) in males was observed at all doses. An increased incidence of dermatosis was observed, with mild dermatitis occurring at the highest dose. Extramedullary haematopoiesis in the spleen and karyomegaly in the liver were observed at an

Endpoints	CAS RN[a]	Effect levels[b]/results
		unspecified dose (NTP 1986).
	68553-00-4	Dermal study: A dose of 8000 mg/kg-bw per day (8 mL/kg per day)[2,h] was applied to male and female New Zealand white rabbits (4 animals per sex) for 5 days, followed by 2 days of rest, followed by 5 more days of exposure. Severe dermal irritation and injury (acanthosis, chronic inflammation, crusting, dermal congestion, dermal oedema and hyperkeratosis) were observed at the application site. Mortality (25%) occurred after a single exposure. Reduced food consumption, slight epithelial hyperplasia of the urinary bladder mucosa (4/8 rabbits), slight centrilobular vacuolar degeneration in the liver (3/8 rabbits) and severe multifocal liver necrosis (7/8 rabbits) were observed (API 1980a, 1980b, 1980c). Dermal study: Doses of 1070, 2140 or 2675 mg/kg-bw per day (1, 2 or 2.5 mL/kg per day)[2,h] were applied to male and female Sprague-Dawley rabbits (4 animals per sex per dose) for 5 days, followed by 2 days of rest, followed by 5 more days of exposure. Significant skin irritation (acanthosis, acute and chronic inflammation, crusting, deep pyoderma, dermal congestion and oedema, hyperkeratosis and epidermal necrolysis) was observed at the treatment site at all doses. Multifocal necrosis and centrilobular vacuolar degeneration of the liver were also observed at all doses (API 1980d).
	68476-33-5	Dermal study: Doses of 496, 992 or 2480 mg/kg-bw per day (0.5, 1.0 or 2.5 mL/kg per day) were applied to male and female Sprague-Dawley rats (10 animals per sex per dose), 5 days per week for 28 days. Minimal reversible dermal irritation was observed at all dose levels. Hyperkeratosis (minimal severity) was observed at the application site at the highest dose. Significant increase in relative liver weight was observed for both sexes at all dose levels. No other substance-related systemic effects were observed (UBTL 1987). Dermal study: Doses of 496, 992 or 1984 mg/kg-bw per day (0.5, 1.0 or 2.0 mL/kg per day)[2,i] were applied to male and female Sprague-Dawley rats (10 animals per sex per dose), 5 days per week for 4 weeks. Mild histopathologic dermal lesions (acanthosis and hyperkeratosis) were observed at 1984 mg/kg-bw in both sexes. Possible dose-related decrease in body weight gain was observed in males (decrease at 992 mg/kg-bw and statistically significant decrease at 1984 mg/kg-bw). Test substance-related anemia was observed, as indicated by increased absolute and relative spleen weights in combination with the absence of abnormal pathological spleen appearances, as well as decreased red blood cell

Endpoints	CAS RN[a]	Effect levels[b]/results
		indices (erythrocyte count, hematocrit (%) and hemoglobin levels), at all three dose levels in both sexes (UBTL 1988).
	64741-62-4	Dermal LOAEL (short-term) = 1 mg/kg-bw per day for dose-related decreases in maternal body weight gain, body weight, food consumption and gravid uterine weight, as well as the occurrence of red vaginal exudates. Doses of 0.05, 1.0, 10, 50 or 250 mg/kg-bw per day were applied to the clipped skin of pregnant CD rats from gestational days 0 to 19 (Hoberman et al. 1995). Other dermal study (short-term): Doses of 8, 30, 125 or 500 mg/kg-bw per day or 4, 30, 125 or 500 mg/kg-bw per day were applied to the shaved backs of pregnant Sprague-Dawley rats (15 animals per dose) from gestational days 0 to 19 (4 mg/kg-bw per day dose given as 8 mg/kg-bw every other day). Aberrant serum chemistry, decreased body weight gain and food consumption, as well as vaginal discharge, were observed at 8 mg/kg-bw per day (applied every other day) (Mobil 1990; Feuston et al. 1997).
	64741-81-7	Other dermal study (short-term): Doses of 8, 30, 125 or 250 mg/kg-bw per day were applied to the shaved backs of pregnant Sprague-Dawley rats (15 animals per dose) from gestational days 0 to 19. At 8 mg/kg-bw per day, decreased thymus weights (relative and absolute), increased liver weights (relative) and skin irritation (dose-related) were observed. Altered haematology parameters and aberrant serum chemistry occurred at an unspecified dose, as well as dose-related skin irritation. Red vaginal discharge, paleness and emaciation were observed at 30 mg/kg-bw per day. Moribundity was observed at 250 mg/kg-bw per day (Mobil 1994a).
	64741-62-4	Dermal LOAEL (subchronic) = 8 mg/kg-bw per day for increased relative liver weight (male and female rats) and increased absolute liver weight (female). Doses of 8, 30, 125, 500 or 2000 mg/kg-bw per day were applied to the shorn backs of Sprague-Dawley rats, 5 times per week for 13 weeks. Increased mortality, decreased body weights, decreased thymus weight and aberrant serum chemistry and haematology were also observed at unspecified doses (Feuston et al. 1994). Dermal LOAEL (subchronic) = 8 mg/kg-bw per day for a significant reduction in platelet count. Doses of 8, 30, 125 or 500 mg/kg-bw per day were applied to the shaved backs of male and female Sprague-Dawley rats (10 animals per sex per dose), 5 times per week for 13 weeks. Increased liver weight was observed for males and females at 30 mg/kg-bw per day and

Endpoints	CAS RN[a]	Effect levels[b]/results
		125 mg/kg-bw per day, respectively. At 30 mg/kg-bw per day (male) and 125 mg/kg-bw per day (female), dose-related reductions in red blood cell, haemoglobin, haematocrit and platelet counts, a dose-related decrease in thymus weight, and increased mortality (20% males and 80% females) were also observed. At 125 mg/kg-bw per day, both sexes exhibited decreased body weight gain. All male and female rats died at 125 and 500 mg/kg-bw per day, respectively (Mobil 1988; Feuston et al. 1997).
	64741-81-7	Dermal LOAEL (subchronic) = 8 mg/kg-bw per day for moderate skin irritation (dose-related). Doses of 8, 30 or 125 mg/ kg-bw per day were applied to the shaved backs of male and female Sprague-Dawley rats (10 animals per sex per dose), 5 times per week for 13 weeks. Altered haematology features and decreased thymus weight (relative and absolute), as well as altered serum chemistry were observed at 30 mg/kg-bw per day. Decreased body weight gain (males), increased liver weight (relative and absolute) and a decreased number of lymphoid cells in the thymus were observed at 125 mg/kg-bw per day (Mobil 1994b).
	64741-62-4	Oral LOAEL = ≥ 125 mg/kg for maternal toxicity. A single dose of 2000 mg/kg on either GD 11, 12, 13, 14 or 15 (to profile effects as a function of gestation day) or single doses of 125, 500 or 2000 mg/kg on GD 12 (to profile effects as a function of dose) were administered to pregnant Sprague-Dawley rats. (1) General observations (≥ 500 mg/kg): Red vaginal discharge, perineal staining and decreased stool. (2) Effects versus gestation day (2000 mg/kg): Decreased body weight gain and thymus weight (regardless of exposure day). (3) Effects versus dose (GD 12): Dose-related decrease in body weight gain and thymus weight (Feuston and Mackerer 1996).
Carcinogenicity	**68476-31-3**	**Chronic dermal studies** Doses of 0, 250 or 500 mg/kg-bw (100 µL applied; test substance diluted in acetone) were applied to the clipped dorsal interscapular skin of B6C3F$_1$ mice (49-50 animals per sex per dose) 5 times per week for 103 weeks. High-dose mice were sacrificed early due to severe irritation at the application site. Skin tumour incidence in male mice (squamous cell papillomas or carcinomas combined) occurred at the application site at the high dose (0/49, 0/49 and 3/49 of mice developed tumours, respectively). Incidence in female mice (squamous cell carcinomas only) at the application site was (0/50, 1/45 and 2/48, respectively). Liver tumour incidence in male mice (hepatocellular adenomas or carcinomas combined) was 9/50, 17/48 and 14/49, respectively. Liver tumour

Endpoints	CAS RN[a]	Effect levels[b]/results
		incidence in female mice (hepatocellular adenomas and carcinomas combined) were 4/50, 4/45 and 5/50 (NTP 1986). Doses of 0, 694 or 1111 mg/kg-bw (50 µL at 50% w/v[c,e] or 100%[c,f], respectively) were applied to the clipped interscapular skin of C3Hf/Bd mice (15 animals per sex per dose) 3 times per week for 60 weeks. Of a larger combined group (groups of mice that received 1 of 5 other test substances), 34/360 developed skin tumours. A breakdown of the number of mice that received 68476-31-3 and developed tumours was not provided. Exposure to the negative control resulted in 1/60 mice developing skin tumours (Easley et al. 1982).
	68476-33-5	A dose of approximately 592 mg/kg-bw (25 µl)[c,f,j] was applied to the skin of male C3H/HeJ mice (50 animals per group) 3 times per week for life. Two samples of thermally cracked residual fuel oil, as well as a blend of straight-run and Residual Fuel Oil, were tested. All three samples were concluded to be dermal carcinogens. Skin tumours developed in 16/20 and 26/50 mice for the two thermally cracked samples, with mean latency periods of 96 and 85 weeks, respectively. Skin tumours developed in 30/50 mice for the blended sample, with a mean latency period of 81 weeks. Positive and negative control substances produced expected results (Exxon Biomedical Sciences Inc. 1992).
	64741-62-4	Doses of 8.4, 16.8, 42, 83.8 or 167.6 mg/kg-bw (25 µL of catalytically cracked clarified oil at 1, 2, 5, 10 or 20% in mineral oil)[c,f,k,l] were applied to male C3H mice (50 animals per dose) 3 times per week for life. At 1%, 9/50 exposed mice developed tumours (4 carcinomas, 5 papillomas). At 2%, 34/50 exposed mice developed tumours (30 carcinomas, 4 papillomas with a latency period of 92 weeks). At 5%, 46/50 exposed mice developed tumours (46 carcinomas with a latency period of 61 weeks). At 10%, 48/50 exposed mice developed tumours (47 carcinomas, 1 papilloma with a latency period of 45 weeks). At 20%, all (50/50) exposed mice developed tumours (50 carcinomas with a latency period of 36 weeks). Of the 610 mice tested with the negative control (highly refined mineral oil) from this study and two other similar studies conducted by the same authors, only 2 mice developed benign papillomas and none developed carcinomas (McKee et al. 1990). **Initiation/promotion dermal study** *Initiation*: A dose of 16.8 mg/kg-bw (50 µL of catalytically cracked clarified oil at 1% in toluene)[c,f,l] was applied to groups of male CD mice (30 per group)

Endpoints	CAS RN[a]	Effect levels[b]/results
		for 5 consecutive days. After a 2-week rest period, the promoter phorbol-12-myristate-13-acetate (PMA) was applied 2 times per week for 25 weeks. A significant increase in skin tumour incidence was observed (26/30 exposed mice developed tumours after 16 weeks). *Promotion*: Details of study design not provided. No increase in histologically confirmed tumour incidence. However, a statistically significant increase in the number of mice with gross masses and shortened latency periods were observed, suggesting a possible weak promoting activity (API 1989).
Developmental & reproductive health effects	64741-62-4	Dermal reproductive LOAEL (female) = 1 mg/kg-bw per day for decreased number of live fetuses, increased incidence of resorptions, early resorptions and the percentage of dead or resorbed conceptuses per litter (these effects were dose-related and were observed at doses that were maternally toxic). Doses of 0.05, 1.0, 10, 50 or 250 mg/kg-bw per day were applied to the clipped skin of pregnant CD rats from gestational days 0 to 19. At 1 mg/kg-bw per day, an increased incidence in fetal variations associated with a decrease in fetal body weight was observed, including slight dilation of the lateral ventricles of the brain, moderate dilation of the renal pelvis, bifid thoracic vertebral centrum and decreased average number of ossified caudal vertebrae, metacarpals and hindpaw phalanges (these effects were noted to be reversible delays in development). (Hoberman et al. 1995). Dermal developmental LOAEL = 8 mg/kg-bw for fetal external abnormalities. Doses of 4, 8, 30, 125 or 250 mg/kg-bw per day were applied to the shaved backs of pregnant Sprague-Dawley rats (10 per dose) for gestational days 0–19 (the 4 mg/kg-bw dose was given as 8 mg/kg-bw every other day). At 8 mg/kg-bw per day, external abnormalities in living and dead fetuses, including cleft palate, micrognathia (shortened lower jaw) and kinked tail, were observed. An increased incidence of resorptions, decreased number of viable offspring, reduced fetal size, visceral anomalies and skeletal variations were observed at 30 mg/kg-bw per day. There were no viable fetuses at 250 mg/ kg-bw per day (Feuston et al. 1989; Mobil 1987e). Other dermal study: Doses of 4, 8, 30, 125 or 500 mg/kg-bw per day were applied to the shaved backs of pregnant Sprague-Dawley rats (15 per dose) from gestational days 0 to 19 (4 mg/kg-bw per day dose was administered as 8 mg/kg-bw every other day). At 8 mg/kg-bw per day, an increased incidence of resorptions and a decreased number of viable fetuses was observed (biologically significant). At

Endpoints	CAS RN[a]	Effect levels[b]/results
		30 mg/kg-bw per day, a statistically significant increased incidence of resorptions was observed, as well as decreased fetal body weight. An increased incidence of fetal external, skeletal and visceral anomalies (primarily rib malformations and cleft palate) was observed at 500 mg/kg-bw per day (Mobil 1990; Feuston et al. 1997). Other dermal study: Doses of 8, 30, 125 or 500 mg/kg-bw per day were applied to the shaved backs of male Sprague-Dawley rats (10 per dose), 5 times per week for 13 weeks. Decreased sperm count after 9 weeks of exposure was observed at 500 mg/kg-bw per day (Mobil 1988; Feuston et al. 1997). Oral reproductive and developmental LOAEL = ≥ 125 mg/kg for increased resorptions, decreased fetal body weight and increased incidence of skeletal malformations. Pregnant Sprague-Dawley rats were administered 2000 mg/kg on one of gestational days (GD) 11–14 (to generate a profile of teratogenic effects as a function of gestation day). Additionally, 125, 500 or 2000 mg/kg was administered on gestational day 12 (to generate a profile of teratogenic effects as a function of dose). Test samples were clarified slurry oil and syntower bottoms. (1) Teratogenic effects per gestation day (2000 mg/kg): The greatest incidence of resorptions/decreased litter size occurred on GDs 11–12. Fetal body weights were reduced on all GDs. The greatest incidence of fetal external anomalies and visceral malformations occurred on GDs 12–14 and 12–13, respectively. Various fetal skeletal malformations occurred on all GDs. (2) Teratogenic effects per dose (GD 12): There was a dose-related response for increased resorptions, decreased litter size, decreased fetal body weight and increased incidence of fetal skeletal malformations. A variety of fetal external anomalies were also observed at 2000 mg/kg (Feuston and Mackerer 1996).
Genotoxicity – *in vivo*	64741-62-4	**Unscheduled DNA Synthesis** Groups of male Fischer 344 rats (3 animals per dose) were administered by oral gavage a single dose of 50, 200 or 1000 mg/kg-bw of test substance, 2 or 12 hours before sacrifice. A significant increase in UDS in primary hepatocyte cultures was observed at 200 mg/kg-bw (after 12 hours only) and 1000 mg/kg-bw (after 2 and 12 hours) (API 1985a). **Sister Chromatid Exchange** Groups of male and female B6C3F1 mice (5 animals per sex per dose) were administered 400, 2000 or

Endpoints	CAS RN[a]	Effect levels[b]/results
		4000 mg/kg-bw test substance via intraperitoneal injection. A significant increase in sister chromatid exchange (SCE)/metaphase in bone marrow cells was observed at ≥ 2000 mg/kg-bw (male; $P < 0.05$) and at 4000 mg/kg-bw (female; $P < 0.01$). The effect exhibited a positive dose-dependent trend at all doses (API 1985b).
	64742-90-1	**Micronuclei Induction** Groups of CD Swiss mice (10 animals per sex per dose) were administered 1250, 2500 or 5000 mg/kg-bw test substance by oral gavage over 2 days. Another group (15 animals per sex) was administered a single dose of 5000 mg/kg-bw. A significant increase in micronucleated polychromatic erythrocytes was observed at ≥ 1250 mg/kg-bw (males) and at 5000 mg/kg-bw (females) (Khan and Goode 1984).
Genotoxicity – *in vitro*	**68476-31-3**	**Mutagenicity** Test substance was negative in *S. typhimurium* TA1535, TA1537, TA98 and TA100 with and without S9 metabolic activation (NTP 1986). Test substance was negative in *S. typhimurium* TA98 with and without S9 metabolic activation (Schultz et al. 1981). **Inhibition of Morphological Transformation** Test substance was negative in ST-FeSV-infected human foreskin fibroblasts without metabolic activation (Blakeslee et al. 1983).
	68553-00-4	**Mutagenicity** *S. typhimurium* TA1535, TA1538, TA98 and TA100 were exposed with and without S9 metabolic activation (Aroclor 1254-induced rat liver). Mutagenicity was not observed (Vandermeulen et al. 1985). Test substance was also negative in a forward mutation assay using *Chlamydomonas reinhardtii* (Vandermeulen and Lee 1986). **Sister Chromatid Exchange** Chinese hamster ovary cells were exposed with and without S9 metabolic activation (Aroclor 1254-induced rat liver). No increase in SCE was observed (Farrow et al. 1983). **Mouse Lymphoma Assay** L5178Y $TK^{+/-}$ cells were exposed to test substance with and without S9 metabolic activation (Aroclor 1254-induced rat liver). Mutant frequency did not increase (Farrow et al. 1983).
	64741-62-4	**Mouse Lymphoma Assay** L5178Y cells were exposed to sample API 81-15 at

Endpoints	CAS RN[a]	Effect levels[b]/results
		concentrations ranging from 0.061–31.3 nL/mL for 4 hours, with and without S9 rat liver metabolic activation. Toxicity was noted at all levels and survival was < 10% at concentrations above 3.9 nL/mL. Without activation, the test substance was weakly positive at the highest concentration only. With activation, the test substance induced a concentration-related increase in mutant frequency at concentrations > 0.977 nL/mL (API 1985c).
	64741-62-4 / 64741-61-3	**Mutagenicity** *S. typhimurium* TA98 was exposed to DMSO extracts of combined test substances at concentrations of 0.5, 1, 2.5, 5 or 10 µL/plate with S9 metabolic activation (Aroclor 1254-induced rat liver). A concentration-related increase in mutagenic potency was observed, with a mutagenicity index of 130 (Blackburn et al. 1984). Additionally, *S. typhimurium* TA98 was exposed to DMSO extracts (dissolved in cyclohexane) at concentrations of 0.5, 1, 1.5, 2 or 5 µL/plate with S9 metabolic activation (Aroclor 1254-induced Syrian golden hamster liver). A concentration-related increase in mutagenic potency was observed, with a mutagenic index of approximately 58 (Blackburn et al. 1986).
	64742-90-1	**Unscheduled DNA Synthesis** Primary rat hepatocyte cultures derived from F-344 male rat liver were exposed to ethanol dilutions of aromatic pyrolysis oil at concentrations of 0.5, 2, 10 or 60 µg/mL for 18–20 hours (without S9 metabolic activation). A concentration-response was observed for UDS at ≥ 2 µg/mL (Brecher and Goode 1984). **Mutagenicity** Chinese hamster ovary cells were exposed to ethanol dilutions of aromatic pyrolysis oil at concentrations of 32, 64, 96, 128, 175 or 256 µg/mL without S9 metabolic activation (Aroclor-1254 induced rat liver) and 128, 175, 256, 375, 512 or 750 µg/mL with S9 metabolic activation. A repeat experiment was conducted at concentrations of 500, 600 or 750 µg/mL with S9 metabolic activation. Reduced cell count was observed at all concentrations (with and without S9) and significant toxicity was observed at all concentrations with S9. An increase in mutant frequency was definitive at 750 µg/mL with an observed linear concentration-related trend for mutagenicity at lower concentrations. In the repeat experiment, an increase in mutant frequency was observed at 500 µg/mL (and the higher concentrations were toxic). No mutagenic effects were observed without S9 metabolic activation (Papciak and Goode 1984).
	64741-62-4	**Sister Chromatid Exchange** Chinese hamster ovary cells were exposed to the test

Endpoints	CAS RN[a]	Effect levels[b]/results
		substance at concentrations of 5–100 µg/mL without S9 metabolic activation and 100–5000 µg/mL with S9 metabolic activation. An increase in SCE was observed with activation. No increase in SCE observed without activation (API 1985e). **Cell Transformation** BALB/3T3 mouse embryo cells were exposed to the test substance at concentrations of 1, 3, 6 or 9 µg/mL without S9 metabolic activation (for 3 days) or 10, 30, 100 or 300 µg/mL with S9 metabolic activation (for 4 days). S9 was prepared from Aroclor-induced male rat liver. An increase in the frequency of transformation was observed at 100 µg/mL after 4 hours. Low survival rates were observed at 300 µg/mL. No increase in morphological transformation without activation (API 1986b).

[a] Studies investigating Fuel Oil No. 4, Fuel Oil No. 6 and Residual Fuel Oil have their CAS RNs indicated in bold.
[b] LC_{50}, median lethal concentration; LD_{50}, median lethal dose; LOAEC, lowest-observed-adverse-effect concentration; LOAEL, lowest-observed-adverse-effect level; NOAEC, no-observed-adverse-effect concentration; NOAEL, no-observed-adverse-effect level.
[c] Body weight (bw) not provided, laboratory standards from Salem and Katz, Inhalation Toxicology, 2006 were used.
[d] This formula is used to convert provided values into mg/kg-bw: *x* mg / *x* bw (in kg).
[e] This formula is used to convert provided values into mg/kg-bw:
50% w/v = 50 g / 100 mL
50 g / 100 mL = *x* / 0.05 mL (dose given to the test animal)
x = 0.025 g = 25 mg of test substance given to the test animal
mg/kg-bw = 25 mg / *x* bw (in kg)
[f] This formula is used to convert provided values into mg/kg-bw: (% of dilution × *x* mL × ρ) / *x* bw.
[g] Densities provided from European Commission c2000b.
[h] This formula is used to convert provided values into mg/kg-bw: *x* mL/kg-bw × ρ.
[i] Density provided from API 2004 (1 mL/kg-day dose corresponded to 992 mg/kg-bw per day).
[j] Density provided from Hess 2006c.
[k] Density not provided; a density from CONCAWE 1998 was used.
[l] A volume/volume dilution was assumed.